analytical sample, mp 125–125.5°, which had an infrared spectrum identical with III free base prepared by method A.

Anal. Calcd for $C_{11}H_{14}N_2SO$: C, 59.43; H, 6.35; N, 12.60; S, 14.42. Found: C, 59.93; H, 6.60; N, 12.69; S, 14.73.

3-(β-Chlorophenethyl)-2-iminothiazolidine Hydrochloride (IV).—To a stirred slurry of 40.0 g (0.154 mol) of III and 62 ml of methylene chloride was added 17 ml (28.4 g, 0.238 mol) of thionyl chloride over a period of 2–3 min. The reaction mixture was stirred for 45 min, filtered, washed with methylene chloride and ether, and dried. The crude product weighed 30.0 g (91%): mp 178–182° and 240°; $\lambda_{\max}^{\text{MeOH}}$ 295 mμ. Recrystallization of the product from ethanol gave 25.3 g (59%) of white crystals, mp 245–246°. Tlc analysis (silica gel) in the solvent system acetonitrile–ammonium hydroxide (95:5, v/v) revealed a major component at R_f 0.80 and a very minor component at R_f 0.85 in both crude and recrystallized product. The minor component had the same mobility as V.

Anal. Calcd for $C_{11}H_{14}N_2SCl_2$: C, 47.66; H, 5.09; N, 10.11; S, 11.56; Cl, 25.58. Found: C, 47.06; H, 4.67; N, 9.37; S, 10.72; Cl, 23.41.

An aqueous solution of the hydrochloride was treated with sodium perchlorate to give the perchlorate salt, mp 206–207°, homogeneous by tlc.

Anal. Calcd for $C_{11}H_{14}N_2SCl_2O_4$: C, 38.72; H, 4.14; N, 8.21; S, 9.40; Cl, 20.78. Found: C, 38.90; H, 4.19; N, 8.01; S, 9.50; Cl, 21.06.

2-Imino-3-*trans*-styrylthiazolidine Perchlorate and Hydrochloride (V).—The following procedure was adapted from that used for the dehydrobromination of α-bromo ketones.[16]

A mixture of 16.0 g (0.0583 mol) of IV, 4.24 g (0.10 mol) of lithium chloride, and 130 ml of dry dimethylformamide was stirred at 113–120° for 3.5 hr, and then at room temperature for 16 hr. The mixture was poured into 1 l. of water and 450 ml of ether and ammonium hydroxide was added to a pH of 8–9. The aqueous layer was extracted again with 450 ml of ether, the ether extracts were washed with water, and dried over anhydrous potassium carbonate. Removal of the solvent *in vacuo* gave 9.43 g of a colorless oil.

The hydrochloride salt was prepared with ethanolic hydrogen chloride. The crude yellow gummy hydrochloride from evaporation of the solvent was warmed with 700 ml of water and filtered; the filtrate was treated with an aqueous solution of 7.35 g (0.06 mole) of sodium perchlorate to precipitate the perchlorate which, after filtering, washing with water, and drying under vacuum, weighed 5.83 g, mp 210–214°. Two recrystallizations from absolute ethanol gave the analytical sample, mp 232.5–234°.

Anal. Calcd for $C_{11}H_{13}N_2SClO_4$: C, 43.35; H, 4.30; N, 9.19; S, 10.52; Cl, 11.63. Found: C, 43.15; H, 4.31; N, 8.98; S, 10.67; Cl, 11.64.

The perchlorate was converted into the free base with ammonium hydroxide and extracted into chloroform. Evaporation of the chloroform, solution in methanol, and the addition of ethanolic hydrogen chloride gave the hydrochloride as cream-colored crystals, mp 224–225°. Recrystallization from methanol–ethanol gave the analytical sample as white needles, mp 223–224°. This had the same tlc mobility as the minor component of IV.

Anal. Calcd for $C_{11}H_{13}N_2SCl$: C, 54.87; H, 5.44; N, 11.64; S, 13.32; Cl, 14.73. Found: C, 54.84; H, 5.40; N, 11.62; S, 13.62; Cl, 14.96.

6-Phenyl-2,3,5,6-tetrahydroimidazo[2,1-*b*]thiazole Hydrochloride (VI).—A slurry of IV prepared from 7.77 g (0.030 mol) of III and 3.21 ml (0.045 mol) of thionyl chloride in 68 ml of methylene chloride (see the preparation of IV) was poured into ice and water and made basic by the careful addition of 3 *N* sodium hydroxide solution. The layers were separated, the aqueous layer extracted with 50 ml of methylene chloride, the organic phase washed with water, and the solvent removed at reduced pressure. The residual free base of IV was refluxed in 100 ml of isopropyl alcohol for 50 min to effect ring closure. The resultant hydrochloride precipitate was filtered, washed with ether, and dried to give 3.22 g of light yellow crystals, mp 255–259° (lit.[2] mp 260–270°). The mother liquor upon treatment with isopropyl alcoholic hydrogen chloride and concentration at reduced pressure gave an additional 2.43 g. The total crude yield was 78%. Recrystallization of the combined fractions from ethanol gave 4.30 g (59%) of product, mp 260–262°.

Registry No.—I, 15591-40-9; IIb, 15591-46-5; III, 15591-41-0; III free base, 15591-42-1; IV, 15643-70-6; IV perchlorate salt, 15643-71-7; V, 15591-43-2; V perchlorate salt, 15591-44-3; VI, 5086-74-8.

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[16] (a) D. Djerassi, N. Finch, R. C. Cookson, and C. W. Bird, *J. Amer. Chem. Soc.*, **82**, 5488 (1960); (b) R. Joly and J. Warnant, *Bull. Soc. Chim. Fr.*, 367 (1958).

New Heteroaromatic Compounds. XXIX.[1] The Mechanism of Salt Formation in Some Nitroborazarophenanthrenes[2]

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The mechanism of salt formation in 6- and 8-nitro-10-methyl- and -10-hydroxy-10,9-borazarophenanthrene[4] has been studied, using ir and ^{11}B nmr[5] spectroscopy, and their pK_A's have been measured. These borazaro derivatives differ from most other analogous compounds[5] in that they behave as Lewis acids, salt formation involving addition of base to boron rather than loss of a proton from OH or NH. Their pK_A's are surprisingly low, comparable with that of phenol, and their longest wavelength absorption bands show large bathochromic shifts on salt formation.

In the course of another investigation, we noticed that 6- and 8-nitro-10-hydroxy-10,9-borazarophenanthrene (Ia and IIa, respectively) both developed intense colors on treatment with alkali, implying that in their conjugate bases there is an enhanced mesomeric interaction between the imino nitrogen and the nitro group *ortho* or *para* to it.

In a prior paper[4] of this series, we reported studies of salt formation in a number of compounds containing the groups BOH, using ^{11}B nmr. The results established that compounds of this type behave as Lewis acids, rather than protic acids, unless the boron atom forms part of an aromatic ring. When the boron atom does form part of an aromatic ring, as in the case in 10-hydroxy-10,9-borazarophenanthrene (IIIa), salt formation normally involves loss of a proton from the hydroxyl group. These results made it difficult to understand the behavior of Ia and IIa, for loss of a proton from hydroxyl would leave an ion (IV) in which the negative charge should be mainly localized

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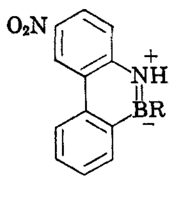
[1] Part XXVIII: M. J. S. Dewar and R. Jones, *J. Amer. Chem. Soc.*, in press.

[2] This work was supported by a grant from the Robert A. Welch Foundation.

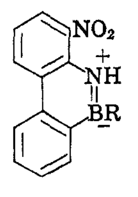
[3] Robert A. Welch Postdoctoral Fellow.

[4] M. J. S. Dewar and V. P. Kubba, *Tetrahedron*, **7**, 213 (1959).

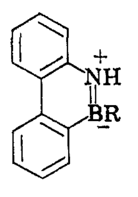
[5] M. J. S. Dewar and R. Jones, *J. Amer. Chem. Soc.*, **89**, 2408 (1967).



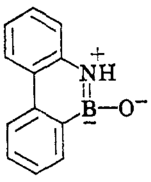
Ia, R = OH
b, R = CH_3



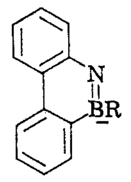
IIa, R = OH
b, R = CH_3



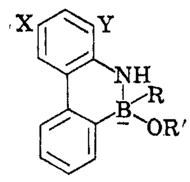
IIIa, R = OH
b, R = CH_3



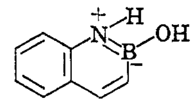
IV



V



VI, X = Y = NO_2 or H
R = OH or CH_3
R′ = H or CH_3



VII

on oxygen and in which one would not therefore expect any large change in the $NH-NO_2$ interaction.

The position was made even more intriguing by the observation that the 10-methyl derivatives, Ib and IIb, also gave colors on treatment with alkali, which seemed to suggest that the conjugate base had lost protons from the imino groups, being nitro derivatives of the ions V. Such a reaction would, however, be surprising in the case of Ia or IIa, since it would require the proton in an imino group to be more acidic than one in hydroxyl.

We therefore measured the ^{11}B nmr spectra of I and II, both in neutral solution and in the presence of excess sodium hydroxide or sodium methoxide, with the results shown in Table I.

TABLE I

^{11}B CHEMICAL SHIFTS OF I AND II UNDER NEUTRAL AND ALKALINE CONDITIONS

Compd	Solvent	Base	Chemical shift,[a] δ	$\Delta\delta$[b]	Line width at half-height, Hz
Ia	Dimethyl sulfoxide	None	−36.9		1250
		OH^-	−12.5	24.4	780
		OCH_3^-	−8.7	28.2	565
Ib	Tetrahydrofuran	None	−38.2		443
		OH^-	−20.0	18.2	394
		OCH_3^-	−11.3	26.9	283
IIb	Tetrahydrofuran	None	−41.0		380
		OH^-	−21.5	19.5	310
		OCH_3^-	−11.4	29.6	207

[a] Chemical shift in parts per million (ppm) relative to ether-boron trifluoride complex. [b] Change in chemical shift in passing from neutral to alkaline solution.

No signals could be obtained from Ia, presumably because the line was too broad; the signals for the other compounds all showed very large upfield shifts on addition of alkali, together with significant decreases in line width. These results indicate unambiguously[5] that salt formation in Ia, Ib, and IIb in each case involves addition of base to boron, rather than loss of a proton from oxygen or nitrogen, the resulting anions being of the type VI.

This conclusion was confirmed by comparisons of the ir spectra of I and II under neutral and basic conditions. The 10-hydroxy derivatives (Ia and IIa) were studied as free acids, and as salts with sodium methoxide, in potassium bromide disks. The 10-methyl derivatives (Ib and IIb) were studied using matched cells and solvents (dioxane or tetrahydrofuran) that are relatively transparent in the 3–4-kK region, with and without addition of sodium methoxide. The results are shown in Table II. In all cases, a strong NH band was observed at 3.3–3.4 kK, showing that salt formation did not involve the imino group. In the case of Ia and IIa, the BOH hydroxyl band at *ca.* 3.5 kK also persisted in the salt. For comparison, the spectrum of 10-methyl-10,9-borazarophenanthrene (IIIb) was also measured.

TABLE II

INFRARED SPECTRA OF I AND II AS FREE ACIDS AND AS SALTS

Compd	Conditions	NH stretch, K	OH stretch, K
IIIb	KBr disk	3390	
Ib	KBr disk	3370	
	Dioxane	3300	
	Dioxane–$NaOCH_3$	3310	
IIb	KBr disk	3370	
	Tetrahydrofuran	3375	
	Tetrahydrofuran–$NaOCH_3$	3376	
Ia	Ia in KBr disk	3320	3560
	Salt ($NaOCH_3$) of Ia in KBr disk	3370	3500
IIa	IIa in KBr disk	3355	3540
	Salt ($NaOCH_3$) of IIa in KBr disk	3375	3550

The proton nmr spectra of Ib and IIb were also measured under neutral and alkaline conditions, using acetone-d_6 as solvent. Progressive addition of sodium methoxide led to a progressive upfield shift of the BCH_3 resonance until a limiting value was reached, corresponding presumably to the total conversion of the parent compounds, in which boron is more or less neutral,[6] into the ions (VI) in which boron carries a formal negative charge. The magnitude of the shifts (0.9 and 1.1 ppm for Ib and IIb, respectively) again provides strong evidence that salt formation involves attachment of base to boron.

Table III records pK_A values for these compounds, together with data for the band of lowest frequency in the uv-visible spectrum. It should be added that IIIb failed to react with sodium methoxide in methanol, being, as expected, a much weaker acid than I or II.

It will be seen that salt formation leads to a very large bathochromic shift (>100 nm) and that the compounds are quite acidic, their pK_A resembling that of phenol. This is in marked contrast to simple hydroxyborazaro compounds such as IIIa or 2-hydroxy-2,1-borazaronaphthalene (VII) which are very weak acids; VII for example is not significantly more

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[6] Although dipolar resonance structures are written for these compounds to emphasize their aromatic nature and relationship to phenanthrene, the net formal charge in boron is almost certainly quite small. This is indicated by the low dipole moment of 10-methyl-10,9-borazarophenanthrene (0.16 D) [R. Huisgen, I. Ugi, I. Ziegler, and H. Huber, *Tetrahedron*, **15,** 44 (1961)] and by detailed SCF MO calculations which will be reported elsewhere in due course.

TABLE III

FIRST ABSORPTION BANDS AND pK_A FOR I AND II

Compd	pK_A	Solvent for spectroscopic measurement	First absorption band	
			P_{max}, nm	Log ε
IIIb		95% EtOH	327	4.014
Ib	9.65	95% EtOH	345	4.021
		95% EtOH + excess OH^-	457	4.253
IIb	9.80	95% EtOH	375	3.754
		95% EtOH + excess OH^-	514	3.954
Ia	9.64	95% EtOH	352	3.928
		95% EtOH + excess OH^-	465	4.212
IIa	9.01	95% EtOH	390	3.697
		95% EtOH + excess OH^-	495	3.939

acidic than water.[7] These results show unequivocally that there must be strong π bonding between boron and nitrogen in compounds such as III, corresponding to significant participation by the dipolar resonance structures written above, as otherwise introduction of nitro groups would not have such a large effect on the Lewis acidity of the boron, nor would salt formation by addition to boron have such a large effect on the absorption spectrum. Introduction of a nitro group leads to cross conjugation, with consequent decreases in the π-electron density on boron and in the mesomeric stabilization of the boron-containing ring; both these effects should increase the Lewis acidity of boron. Likewise addition of base to boron removes it from conjugation with the adjacent imino nitrogen, thus greatly increasing the interaction of the latter with an *ortho* or *para* nitro group. It is true that the nitro group should also indirectly increase the acidity of the hydroxylic protons in Ia or IIa by making the boron atom more positive; the change in acidity of the proton should, however, be much less than that of boron, so it is not surprising that Ia and IIa behave as Lewis acids, while IIIa behaves as a protic one.

The conclusion that the B–N π bonds in compounds such as III must be strong is not surprising in view of clear evidence that such compounds are aromatic.[8]

In conclusion, it might be remarked that the color changes shown by these compounds on treatment with base are very marked and that they might therefore prove useful as indicators; the alkaline solutions of Ia and IIa in particular are quite stable, and the color change in the case of Ia is particularly intense.

Experimental Section

Compounds I and II were prepared by nitration of III, and of the analogous 10-methyl derivative, as described previously,[4] these in turn being obtained by the procedure of Dewar, Dewar, and Gaibel.[9]

The pK_A measurements were carried out spectrophotometrically by the method of Perkampus and Rossel.[10]

Registry No.—Ia, 15813-11-3; Ib, 15856-52-7; IIa, 15889-55-1; IIb, 15813-12-4; IIIb, 15813-13-5.

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[7] R. Dietz, Ph.D. Thesis, Queen Mary College, University of London, 1960.

[8] See M. J. S. Dewar, *Prog. Boron Chem.*, **1**, 235 (1964).

[9] M. J. S. Dewar, R. B. K. Dewar, and Z. L. F. Gaibel, *Org. Syn.*, **46**, 65 (1966).

[10] H. H. Perkampus and T. Rossel, *Z. Electrochem.*, **60**, 1102 (1956).

The Synthesis of 6-Substituted Thieno[3,2-*b*]pyrroles[1,2]

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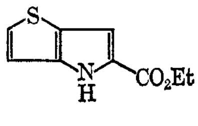
The synthetic pathway to 5-carbethoxythieno[3,2-*b*]pyrrole has been improved and a new product isolated from its reaction with formaldehyde and dimethylamine. Several 6-substituted 5-carbethoxythieno[3,2-*b*]pyrrole compounds have been hydrolyzed and decarboxylated under mild conditions to afford important intermediates for the preparation of thieno[3,2-*b*]pyrrole analogs of natural indole compounds.

In a recent paper, the preparations of 5-carbethoxythieno[3,2-*b*]pyrrole (I) and a number of its 6-substituted derivatives were reported.[4] In a continuing effort to prepare 6-substituted derivatives of thieno[3,2-*b*]pyrrole which would be analogous to naturally occurring 3-substituted indole compounds, a study of the hydrolysis and decarboxylation of several of these disubstituted thieno[3,2-*b*]pyrroles has been undertaken. Moreover, the synthetic pathway to I has been improved and a new product isolated from its reaction with formaldehyde and dimethylamine.



I

A key intermediate in the preparation of I and in the first synthesis of thieno[3,2-*b*]pyrrole[5] was 2-methyl-3-nitrothiophene (V) which was obtained in 16% over-all yield from 2,5-dibromothiophene. This same intermediate has also been prepared in 14% over-all yield from 2-methylthiophene (II) by successive chlorosulfonation, nitration, and dechlorosulfonation reactions.[6] By adapting the method of Siedel and Sturn[7] for the chlorosulfonation reaction and the method of Carpanelli and Leandri[8] for the nitration reaction, the latter process has been improved to give 2-methyl-3-nitrothiophene in

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[1] Supported in part by a research grant (CA-8663) from the National Cancer Institute, U. S. Public Health Service.

[2] Abstracted in part from a thesis submitted by R. L. Keener to the Graduate College of the University of Illinois, Urbana, Ill., in partial fulfillment of requirements for the degree of Doctor of Philosophy, 1967.

[3] (a) National Science Foundation Summer Fellow, 1964; (b) Phillips Petroleum Co. Fellow, 1965–1966.

[4] W. W. Gale, A. N. Scott, and H. R. Snyder, *J. Org. Chem.*, **29**, 2160 (1964).

[5] H. R. Snyder, L. A. Carpino, F. Zack, Jr., and J. F. Mills, *J. Amer. Chem. Soc.*, **79**, 2556 (1957).

[6] C. Sone and Y. Matsuki, *Nippon Kagaku Zasshi*, **83**, 496 (1962).

[7] W. Siedel and K. Sturn, German Patent 1,088,509; *Chem. Abstr.*, **56**, 456*f* (1962).

[8] C. Carpanelli and G. Leandri, *Ann. Chim.* (Rome), **51**, 181 (1961).