Boron Photochemistry. V. Photochemical Syntheses of the Borazarophenanthrene, Boroxarophenanthrene, and Borathiarophenanthrene Ring Systems

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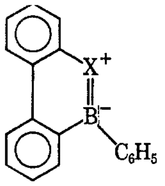
The 2-iodo-substituted anilino- and phenoxyboranes resulting from the reaction between chlorodiphenylborane and 2-iodoaniline and 2-iodophenol, respectively, have been photocyclized in cyclohexane solution to the corresponding phenylborazaro- and phenylboroxarophenanthrenes. A similar reaction with 2-iodothiophenol has yielded the 10-phenyl derivative of the recently reported 10,9-borathiarophenanthrene ring system.[1] This system is considerably less stable toward base than the corresponding borazaro- or boroxarophenanthrene systems, although ultraviolet spectral evidence indicates a delocalized π-electron system.

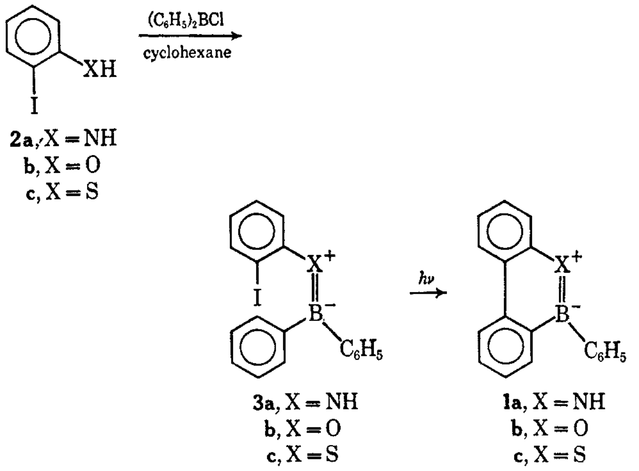
In previous studies we have examined the photochemistry of tetraaryl boron compounds and complexes formed between triarylboranes and electron-donating species.[2,3] In contrast to the triarylboranes, these tetrahedral molecules are photochemically reactive. For example, on photolysis, sodium tetraphenylborate yields biphenyl and phenylcyclohexadienes by an intramolecular reaction,[2a] whereas triphenylborane is inert.[2b] Of interest in connection with this study was the photochemistry of the borazarophenanthrene system (**1a**). In this system the boron atom adopts an sp^2 configuration but the molecule resembles the tetrahedral complexes mentioned earlier in that there is a high electron density around the boron atom due to donation from the adjacent nitrogen atom. However, **1a** proved to be extremely stable to photolysis under a variety of conditions, which prompted us to consider possible photochemical routes to **1a** and the related boron-containing heterocyclic systems, **1b** and **1c**. Previously the borazarophenanthrene system (**1a**) and its derivatives have been prepared from 2-aminobiphenyls.[4,5]



1a, X = NH
b, X = O
c, X = S

Recently, Kupchan and Wormser described the photochemical conversion of iodostilbenes into phenanthrenes.[6] We therefore studied the reactions shown in Scheme I.

SCHEME I



Treatment of 2-iodoaniline (**2a**) with chlorodiphenylborane was assumed to yield **3a**. Irradiation of the solution yielded the desired compound, **1a**, identical in every respect with an authentic sample.[4] Excess iodoaniline was used to absorb the hydrogen chloride released during the formation of **3a**. Similarly, **2b** yielded boroxarophenanthrene **1b**, identical with an authentic sample.[7] Under similar conditions the conversion of **2c** into **1c** failed. Although the borathiarophenanthrene system has not been described, we were unable to detect a parent ion in the mass spectrum of the crude irradiation product corresponding to that expected for **1c**. However, the reactions between thiols and chloroboranes tend to be incomplete.[8] We therefore studied the reaction sequence in the presence of 2,6-lutidine. This modification resulted in the formation of the desired 10-phenyl-10,9-borathiarophenanthrene (**1c**). The assignment of such a structure rests on method of synthesis and analytical and spectroscopic data. Figure 1 shows the close correspondence between the ultraviolet spectra of **1a** and **1c**. Compound **1c** showed a parent ion of *m/e* 272 in its mass spectrum, as required for the proposed structure. The effect of 2,6-lutidine on the formation of **1a** and **1b** has been studied briefly. In the formation of **3**, hydrogen chloride is evolved, and, in the photocyclization, hydrogen iodide is evolved. We were interested in learning if the yield of the desired products could be improved by trapping these hydrogen halides. Table I summarizes the variations we have studied.

The increased yields of the heterocycles in the presence of a twofold excess of chlorodiphenylborane

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(1) After the preparation of this manuscript the synthesis of bis(10,9-borathiarophenanthryl) ether was described [F. A. Davis and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **90**, 3511 (1968)]. The B–S bond in the 10-phenyl-10,-9-borathiarophenanthrene reported here appears to be considerably more stable toward hydrolysis than that in the ether. We encountered no problems in obtaining the ultraviolet spectrum in cyclohexane (Figure 1). Even in methanol a diffuse form of the spectrum was recorded.

(2) (a) J. L. R. Williams, J. C. Doty, P. J. Grisdale, R. Searle, T. H. Regan, G. P. Happ, and D. P. Maier, *J. Amer. Chem. Soc.*, **89**, 5153 (1967); (b) J. L. R. Williams, P. J. Grisdale, and J. C. Doty, *ibid.*, **89**, 4538 (1967).

(3) J. L. R. Williams, J. C. Doty, P. J. Grisdale, T. H. Regan, G. P. Happ, and D. P. Maier, *ibid.*, **90**, 53 (1968).

(4) M. J. S. Dewar, V. P. Kubba, and R. Pettit, *J. Chem. Soc.*, 3073 (1958).

(5) M. J. S. Dewar and V. P. Kubba, *J. Org. Chem.*, **25**, 1722 (1960).

(6) S. M. Kupchan and H. C. Wormser, *ibid.*, **30**, 0792 (1965).

(7) M. J. S. Dewar and R. Dietz, *J. Chem. Soc.*, 1344 (1960).

(8) G. E. Coates and K. Wade, "Organometallic Compounds," Vol. 1, "The Main Group Elements," Methuen and Co. Ltd., London, 1967, p 284.

Table I

Dependence of the Yield of the Heterocyclic Compounds on the Reactant Composition

Run	Iodo derivative Compd	(mmol)	$(C_6H_5)_2BCl$, mmol	2,6-Lutidine, mmol	Time for max yield, hr	Yield,[a] Compd	%
1	**2a**	(10)	5		4	**1a**	35
2	**2a**	(15)	5		4.5	**1a**	49
3	**2a**	(10)	5	5	4.5	**1a**	39
4	**2a**	(5)	5	5	5	**1a**	49
5	**2a**	(5)	10	10	10	**1a**	80[b]
6	**2b**	(5)	5		4.5	**1b**	43
7	**2b**	(5)	5	5	5	**1b**	42
8	**2b**	(5)	5	10	5	**1b**	37
9	**2b**	(5)	10	10	6	**1b**	43[b]
10	**2c**	(5)	5		5	**1c**	0
11	**2c**	(5)	5.5	10	5	**1c**	41
12	**2c**	(5)	10	10	4	**1c**	91[b]

[a] These are yields calculated from spectral data. [b] Yields of isolated materials are quoted for these runs in the Experimental Section.

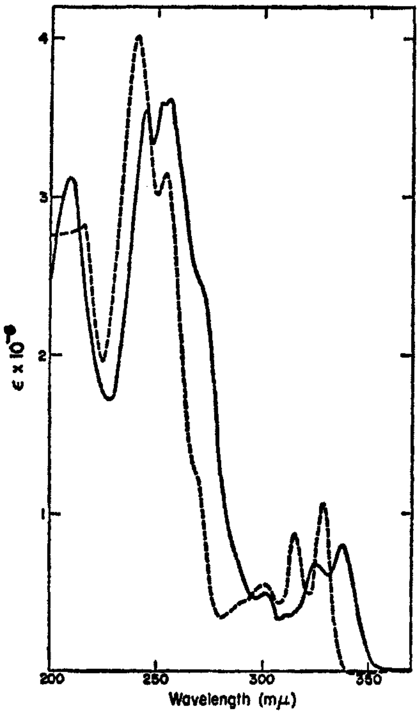
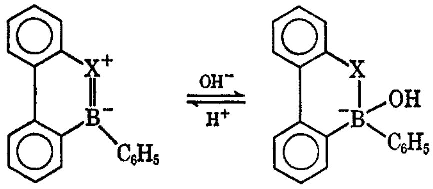


Figure 1.—Ultraviolet spectra of 10-phenyl-10,9-borazarophenanthrene (- - -) and 10-phenyl-10,9-borathiarophenanthrene (——) in cyclohexane.

was unexpected. Such an excess either increases the yield of the intermediates, **3**, or may serve as a trap for residual traces of water, even though very thorougn precautions were taken to exclude all water.

During this study we have observed that the stabilities of the heterocyclic ring systems decrease in the order **1a** > **1b** > **1c**. We were surprised when, during the work-up of the photochemical reaction mixture containing **1b**, compound **1b** was extracted from a cyclohexane solution with 1% sodium hydroxide solution. Studies with authentic **1b** revealed that it could be completely removed from a cyclohexane solution with 1% sodium hydroxide solution but 78% could be recovered by acidification of the aqueous solution (glpc analyses). These results suggest the equilibrium shown below to be similar to that reported for the B–OH derivative.[9] Spectroscopic evidence supports this interpretation. When sodium hydroxide solution was added to a methanol solution of **1b**, one band centered at 316 mμ replaced the characteristic long-wavelength bands of **1b** (323, 305, 294, 283 mμ). These latter reappeared when the solution was acidified. By contrast, **1a** was unaffected, even by 50% sodium hydroxide solution, and **1c** could not be recovered from basic solutions.



1b, X = O
c, X = S

4a, X = O
b, X = S

The close similarity between the spectra of **1a** and **1c** indicates very similar delocalized aromatic systems in these two molecules, and so one would expect similar stabilities. The observed instability of borathia system **1c** toward base can be accounted for in terms of steric effects postulated previously in discussing the stability of the boroxarophenanthrene system.[9] The strain in this system was thought to be relieved by the boron adopting a tetrahedral configuration in the presence of OH^-. The covalent radius of sulfur (1.02 Å) is considerably larger than that of oxygen (0.73 Å). The additional strain imposed by substituting sulfur for oxygen to give **1c** and **4b** could be relieved by cleavage of the B–S bond.

The problem of preparing substituted borazaro-, -oxaro-, or -thiarophenanthrenes now involves the synthesis of the related 2-iodoanilines, -phenols, and -thiophenols. This is much easier, in many cases, than preparing the corresponding biphenyl derivatives.

We are examining the scope of this type of photochemical synthesis of heterocyclic boron compounds. The present synthesis provides a convenient, simple route to a variety of substituted and complex multiring, boron-containing, heterocyclic compounds.

Experimental Section

General.—All melting points are corrected. Spectra were determined with a Cary Model 15 ultraviolet spectrometer and a Perkin-Elmer Infracord spectrometer. Analytical glpc was performed using an F & M Model 5750 gas chromatograph equipped

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(9) M. J. S. Dewar and R. Dietz, *Tetrahedron*, **15**, 26 (1961).

with a 0.25 in. × 10 ft long column packed with 15% OV17 on Chromosorb W. Preparative glpc was performed using an F & M Model 776 gas chromatograph equipped with a 0.75 × 80 in. long column packed with 15% OV17 on Chromosorb W.

Materials.—Eastman Grade 2-iodoaniline and 2-iodophenol were used without further purification. Chlorodiphenylborane was prepared by the method of Niedenzu, Beyer, and Dawson.[10] 2-Iodobenzenesulfonyl chloride was prepared by the method of Schwarzenbach and Egli.[11]

2-Iodothiophenol.—A solution of 200 g (0.88 mol) of stannous chloride dihydrate in 250 ml of concentrated hydrochloric acid was treated over 10 min with a solution of 50 g (0.17 mol) of 2-iodobenzenesulfonyl chloride in 250 ml of acetic acid. The solution was stirred on a steam bath for 2 hr, then steam distilled. The distillate was extracted with dichloromethane, and the extract dried and evaporated to yield the crude thiol. Distillation yielded the pure thiol, 22 g, 56%, bp 117–120° (10 mm) [lit.[11] bp 119.5° (11 mm)]. It was stored at 0° over zinc dust under nitrogen.

Photocyclizations.—The horizontal thin-film photochemical reactor described earlier[12] was used for the preparation of the boron-containing compounds. The apparatus was thoroughly dried under vacuum for 1 hr and filled with dry nitrogen. The iodo compound was then introduced into the flask and the apparatus evacuated and filled with dry nitrogen several times. Approximately 600 ml of dry cyclohexane was then distilled directly from lithium aluminum hydride under nitrogen into the flask. The chlorodiphenylborane and the 2,6-lutidine were injected into the flask, and the contents mixed for 1 hr at room temperature by rotating the flask. The resulting solution was then irradiated using a Hanovia 100-W 608A-36 lamp in a quartz insert. The progress of the reaction was followed by withdrawing 100-μl samples of the photolysis solution. The sample was then diluted with 3 ml of solvent and examined by ultraviolet spectroscopy. Compound **1a** shows a characteristic band at 329 mμ (ε 10,600), **1b** shows a band at 323 mμ (ε 6300), and **1c** shows a band at 338 mμ (ε 7850). When no increase in the intensity of the long-wavelength band was observed, the contents of the flask were removed and washed in sequence with water, dilute hydrochloric acid, water, dilute sodium thiosulfate solution, and water. (Solutions of **1a** were also washed with dilute sodium hydroxide solution.) The organic layer was dried and evaporated to yield the crude product.

10-Phenyl-10,9-borazarophenanthrene (1a).—The crude product from run 5 (see Table I) crystallized as prisms from ligroin (bp 63–75°), 0.65 g, 51%, mp 106–108°, and was identical with an authentic sample.[4]

10-Phenyl-10,9-boroxarophenanthrene (1b).—The crude product (run 9, Table I) was purified by preparative glpc at 280° to yield the pure compound as a white solid, mp 80–82°, 0.35 g, 31%, identical with an authentic sample.[7]

10-Phenyl-10,9-borathiarophenanthrene (1c).—The crude product (run 12, Table I) crystallized from ligroin (bp 63–75°) in pale yellow prisms, 0.7 g, 50%, mp 129–130°.

Anal. Calcd for $C_{18}H_{13}BS$: C, 79.5; H, 4.8; B, 4.0; S, 11.8; mol wt, 272. Found: C, 79.2; H, 5.0; B, 4.0; S, 11.7; mol wt, 272 (mass spectrum).

Registry No.—**1a,** 19393-10-3; **1b,** 19374-73-3; **1c,** 19374-74-4.

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(10) K. Niedenzu, H. Beyer, and J. W. Dawson, *Inorg. Chem.*, **1**, 738 (1962).

(11) G. Schwarzenbach and H. Egli, *Helv. Chim. Acta*, **17**, 1176 (1934).

(12) J. L. R. Williams and P. J. Grisdale, *Chem. Ind.* (London), 1477 (1968).

Observations on the Mechanism of Addition of Iodine Isocyanate to Unsaturated Compounds[1,2]

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Addition of iodine isocyanate to unsaturated compounds has been studied under competitive reaction conditions with pairs of olefins using preformed solutions of iodine isocyanate and also generating it *in situ*. Reactivity series are obtained which not only differ from each other but also from a series derived from kinetic studies (single olefins used) with *in situ* generated iodine isocyanate. When preformed solutions of iodine isocyanate are used the rate depends primarily on its concentration and that of the unsaturated compound, and is approximated by second-order kinetics. When iodine isocyanate is generated *in situ* in the presence of the unsaturated compound, complexation with iodine can play a major role in the mechanism depending on the complexation ability of the unsaturated compound. With poorly complexing but reactive olefins, for example, 2,3-dimethyl-2-butene, the reaction approaches the limiting rate of formation of iodine isocyanate. Most unsaturated compounds, however, react in part with iodine isocyanate directly and in part as iodine–olefin complexes with silver cyanate to form the observed vicinal iodoisocyanates.

In previous articles[4,5] we discussed the relative rates of addition of iodine isocyanate, generated *in situ* from iodine and silver cyanate, to unsaturated compounds. These results showed that *in situ* addition of iodine isocyanate occurs in an electrophilic manner, confirming the same observation, based on stereochemical considerations, by Hassner and Heathcock[6] and Drefahl, Ponsold and Köllner.[7]

Studies by Rosen and Swern[8] have shown that homogeneous, preformed solutions of iodine isocyanate also react in an electrophilic manner. We have now extended these studies to include the competitive reaction of pairs of olefins with preformed and *in situ* generated iodine isocyanate.

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(1) Pseudohalogens. VI. For V, see H. Hamann and D. Swern, *Tetrahedron Lett.*, No. 28, 3303 (1966).

(2) Presented in part at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966. The authors wish to acknowledge the partial support of this work by U. S. Public Health Service Research Grants CA-07803 and CA-07174 of the National Cancer Institute.

(3) Work submitted by C. G. G. in partial fulfillment of the requirements for the Ph.D. degree, and by S. R. for the Master's degree, Temple University, Feb 1967.

(4) C. G. Gebelein and D. Swern, *J. Org. Chem.*, **33**, 2758 (1968).

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(6) A. Hassner and C. Heathcock, *Tetrahedron*, **20**, 1037 (1964); *J. Org. Chem.*, **29**, 3640 (1964); **30**, 1748 (1965); *Tetrahedron Lett.*, 393 (1963); 1125 (1964).

(7) G. Drefahl and K. Ponsold, *Chem. Ber.*, **93**, 519 (1960); G. Drefahl, K. Ponsold, and G. Köllner, *J. Prakt. Chem.*, **23**, 136 (1964).

(8) S. Rosen and D. Swern, *Anal. Chem.*, **38**, 1392 (1966).