Anal. Calcd. for $C_3H_6O_2BCl$: C, 29.94; H, 5.02; Cl, 29.46; B, 8.99. Found: C, 30.76; H, 5.27; Cl, 30.80; B, 8.99.

Distillation of the metaborate (7.02 g.) under reduced pressure gave a fraction (0.6 g.) containing very little boron (*ca.* 0.8%), b.p. 35° (0.05 mm.), and, after prolonged heating, a fraction (3.13 g.), b.p. 100-120° (0.05 mm.), (B content, 4.0%), n_D^{25} 1.4585. This fraction on redistillation gave pure trisester, VI. The residue in the flask (2.0 g.) contained boron, (18.3%).

Reaction of metaborate with I. I (4.7 g.) and 3-chloropropyl metaborate (4.9 g.) were subjected to pyrolysis conditions (100°) for 15 hr. There was no loss of weight. I was recovered (3.4 g., b.p. 20° (0.05 mm.)), and trisester VI (2.7 g.). No trace of the mixed ester Ve was found in this or two checking runs. Reaction of metaborate with 3-chloropropyl dichloroborinate. Metaborate (3.5 g.) and dichloroborinate (4.1 g.) were mixed at −80° and heated at 20° for 90 min. Boron trichloride evolved (0.7 g.) was trapped at −180° (boron: chlorine ratio found 1:9.5; calcd., 1:9.8). Much of the distillate had a wide boiling range, but one sharp fraction (0.6 g., n_D^{25} 1.4575) corresponding to trisester VI was obtained.

Acknowledgment. It is a pleasure to thank Dr. P. J. Hendra for helpful discussions, and Messrs. B. Smethurst and R. Lane for technical assistance. Partial support from the European Research Office, U. S. Department of the Army, is also gratefully acknowledged.

ENGLEFIELD GREEN, SURREY, U. K.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO]

New Heteroaromatic Compounds. XV.[1] Halogenation of 2-Methyl-2,1-borazaronaphthalene

MICHAEL J. S. DEWAR AND ROY DIETZ

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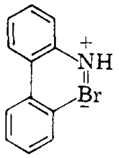
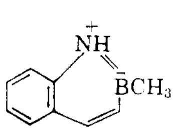
Bromination of 2-methyl-2,1-borazaronaphthalene gives a mixture of the 3-bromo derivative together with *o*-amino-ω-bromostyrene, chlorination gives analogous products. The first step in these reactions seems to be the formation of a π-complex involving the 3,4-bond; the possibility that similar π-complexes may be formed as intermediates in the substitution of other aromatic compounds is discussed.

Derivatives of 10,9-borazarophenanthrene undergo halogenation,[2] nitration,[2] and Friedel-Crafts acetylation[3] in the 6- and 8-positions, as predicted by the simple perturbation form of the MO theory that has proved a good semiquantitative guide to the orientation of substitution in other aromatic systems.[4]

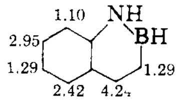
By an unfortunate coincidence the most reactive positions in 10,9-borazarophenanthrenes (I) are those *ortho* and *para* to the imino group; electrophilic attack would therefore be expected to take place preferentially in those positions even if central boron-containing ring were nonaromatic. This difficulty does not arise in the case of 2,1-borazaronaphthalenes, *e.g.*, II.[5] Here one would predict attack mainly in the benzenoid ring if the compound is aromatic, the corresponding π-activation energies[4] being shown in III; the predicted order of reactivity is 8 > 3 = 6 > 5 ⟩⟩⟩ 4. If the compound were nonaromatic, the preferred point of attack should certainly be the styrene-like 3,4-bond and the reaction should lead to addition rather than substitution, particularly for the reactions of II with halogens.



I



II



III

2-Methyl-2,1-borazaronaphthalene was brominated and chlorinated in acetic acid or carbon tetrachloride using standard solutions of halogen to ensure addition of one mole. The uptake of halogen was in all cases rapid and quantitative at room temperature. The nonbasic material was purified by chromatography and yielded in each case only one product, C_9H_9NBS (X = Cl, Br), whose ultraviolet spectrum (Fig. 1) resembled closely that of II. The infrared spectra resembled that of II in the region most characteristic of aromatic substitution (1660–2000 cm.$^{-1}$). It therefore seemed likely that the compounds were the 3-chloro and 3-bromo derivatives of II.

The basic products from the halogenations consisted of compounds C_8H_8NX (X = Cl, Br) whose ultraviolet spectra (Fig. 2) resembled that of 2-aminostyrene, but whose infrared spectra, unlike

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[1] Previous paper, S. S. Chissick, M. J. S. Dewar, and P. M. Maitlis, *J. Amer. Chem. Soc., in press.*

[2] M. J. S. Dewar and V. P. Kubba, *Tetrahedron,* **7**, 213 (1959) *J. Org. Chem.*, **25**, 1722 (1960).

[3] M. J. S. Dewar and V. P. Kubba, *J. Amer. Chem. Soc., in press.*

[4] M. J. S. Dewar, T. Mole, and E. W. T. Warford, *J. Chem. Soc.*, 3581 (1956); M. J. S. Dewar and P. M. Maitlis, *J. Chem. Soc.*, 2521 (1957); M. J. S. Dewar, *J. Amer. Chem. Soc.*, **74**, 3357 (1952).

[5] M. J. S. Dewar and R. Dietz, *J. Chem. Soc.*, 2728 (1959).

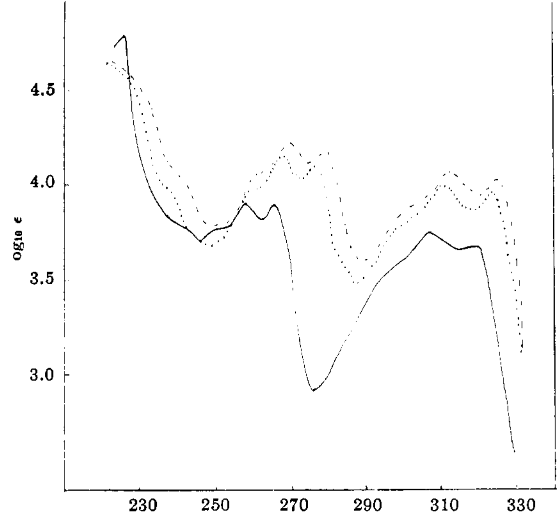
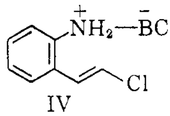
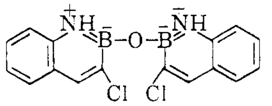
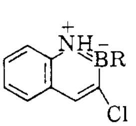


Fig. 1. Comparison of the ultraviolet spectrum of 2-methyl-2,1-borazaronaphthalene (————) with the spectra of its 3-bromo (–·–·–·) and 3-chloro (......) derivatives

that of 2-aminostyrene, showed no absorption (*ca.* 1420 cm.$^{-1}$) attributable to the in-plane vibrations of a $=CH_2$ group. Peaks characteristic of similar deformations of a —CH =C— group (1297, 1300 cm.$^{-1}$), of the out-of-plane CH deformations of a *trans*-substituted double bond (935, 943 cm.$^{-1}$) and of the NH stretchings of a primary amine (935, 3472 cm.$^{-1}$) were present. This suggested that the compounds were ω-substituted 2-aminostyrenes and the chloro derivative indeed proved identical with ω-chloro-2-aminostyrene prepared from 2-nitrocinnamic acid.


IV


V


VIa. R = OCH_3
b. R = CH_3

The 1:1 adduct (IV) of boron trichloride and ω-chloro-2-aminostyrene was prepared in methylene chloride and then heated in dry benzene. Nearly two moles of hydrogen chloride were swept from the apparatus with dry nitrogen, absorbed in water, and determined by titration. That no boron trichloride was lost from IV during this treatment was shown the lack of any further acidity to phenolphthalein when mannitol was added. Hydrolysis of the reaction mixture gave a very good yield of bis(3-chloro-2,1-borazaro-2-naphthyl)ether (V). The structure followed from the method of preparation, elementary analysis and the similarity of the ultraviolet and infrared spectra, which showed no hydroxyl stretching absorption, to those of bis-(2,1-borazaro-2-naphthyl) ether. Crystallization of V from methanol gave 2-methoxy-3-chloro-2,1-borazaronaphthalene (VIa). Treatment of V with excess of methylmagnesium iodide produced 2-methyl-3-chloro-2,1-borazaronaphthalene (VIb), which was identical with the product of the original chlorination. The products of bromination were shown to be ω-bromo-2-aminostyrene and 2-methyl-3-bromo-2,1-borazaronaphthalene by analogy with the chlorination, by elementary analysis, and by the close spectral similarity between the products of chlorination and bromination. The yields of the two products under various conditions are summarized in Table I.

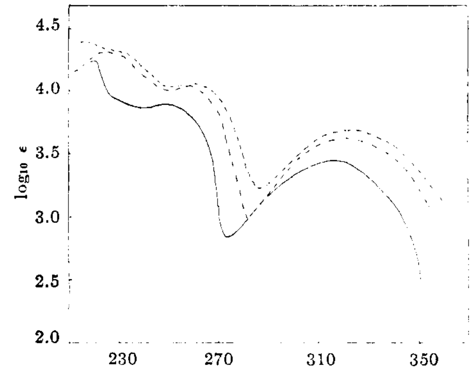


Fig. 2. Comparison of the ultraviolet spectra of *o*-aminostyrene (————) and its ω-bromo (– – – –) and ω-chloro (–·–·–·) derivatives

TABLE I

EFFECT OF CONDITIONS ON THE HALOGENATION OF 2-METHYL-2,1-BORAZARONAPHTHALENE IN ACETIC ACID

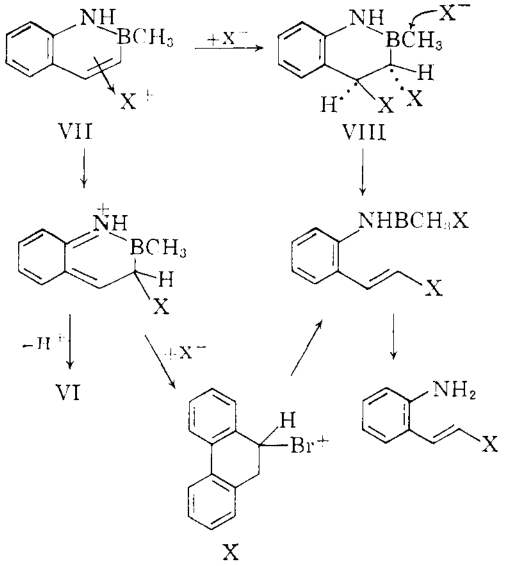
Halogen	Substitution[e]	Deboronation[e]	Yield[e]
Chlorine[a]	25%	67%	92%
Bromine[a]	60	29	89
Chlorine[b]	22	68	90
Bromine[b]	62	29	91
Chlorine[c]	20	66	86
Bromine[c]	56	28	84
Chlorine[d]	8	66	74

[a] With an equimolecular proportion of halogen. [b] With a deficiency (0.7 mole) of halogen. [c] With slower addition (2 hr.) and longer storage (3 hr.) than described. [d] In carbontetrachloride. [e] Yield of product isolated.

The behavior of 2-methyl-2,1-borazaronaphthalene on halogenation therefore differed from that of 10-methyl-10,9-borazarophenanthrene in two respects. The orientation of the attack was not in agreement with the theoretical predictions and deboronation accompanied substitution. Deboronation was a result neither of direct solvolysis of the 3-halogen compounds, as VIb was recovered unchanged after twenty hours solution in acetic acid, nor of attack by the liberated hydrogen halide, as VIb was unchanged after three hours in acetic acid with a large excess of hydrogen chloride. Variation of the time of reaction was without significant effect in both bromination and chlorination, while the use of a deficiency of chlorine produced essentially the same ratio of chlorination to deboronation.

DISCUSSION

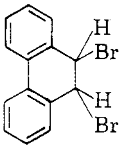
The only reasonable explanation of these results seems to be that the primary attack is on the 3,4-bond with production of the π-complex (VII). This could give rise to the observed products in a variety of ways some of which are indicated below. If the first product of the reaction is a π-complex, one would expect that π-complex to be VII; for II must certainly be less aromatic than naphthalene and so the 3,4-bond must have the highest bond order.



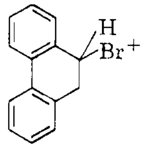
This argument might suggest that II is not an aromatic compound, particularly since the addition product VIII, if formed should undergo a facile concerted elimination as indicated above, a reaction for which there would be many analogies. The fact that no simple addition product was formed cannot therefore be taken as evidence for the aromacity of II.

However, several lines of evidence suggest that the borazaro naphthalenes owe their unusual stability to aromatic resonance[6]; if so, the results reported here might be taken to indicate that the first step in aromatic substitution can be the formation of a π-complex which subsequently rearranges.[7]

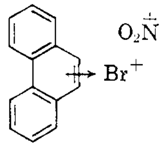
This certainly seems to be the case in the bromination of phenanthrene which gives almost exclusively 9,10-dibromo-9,10-dihydrophenanthrene (IX) by addition to the 9,10-bond.[8] If this were formed *via* the bromophenanthrenonium ion (X) it would be difficult to explain why attack takes place almost exclusively in the 9-position, for theory[4] suggests that the 9- and 1-positions should differ little in reactivity and this was found to be the case for the nitration of phenanthrene in acetic acid.[9] The only reasonable explanation seems to be that the π-complex (XI) is formed and reacts with a bromide ion to form IX.



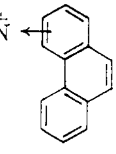
IX



X



XI



XII

The π-complex would not easily lose a proton to form 9-bromophenanthrene unless it first isomerized to X and this may be unfavorable; for Br$^+$ forms very stable π-complexes and the stability of XI should be further enhanced by the very high order of the 9,10-bond in phenanthrene.

One or two other pieces of evidence suggest that π-complexes may often be formed in as intermediates which immediately isomerize to arenonium ions. This would provide an attractive explanation for certain anomalies observed in the nitration of phenanthrene[9] where the yield of 4-isomer was much less, and that of the 3-isomer much more, than predicted.[4] The low yield of the 4-isomer could be ascribed to steric hindrance. If the 4- and 3-isomers are formed from the common π-complex precursor (XII), this steric effect would simultaneously reduce the yield of 4-nitrophenanthrene and increase that of the 3-isomer.

These arguments suggest that the possible role of π-complex intermediates in aromatic substitution deserves re-examination. It can be shown[4] that the predicted orientation should be the same as for the conventionally accepted model even if the π-complexes are formed irreversibly, each π-complex isomerizing only to one of two possible arenonium ions.

EXPERIMENTAL

2-Methyl-2,1-borazaronaphthalene was prepared from bis-(2,1-borazaro-2-naphthyl) ether.[10] Chlorine was dried with concentrated sulfuric acid. Bromine was purified by shaking with concentrated sulfuric acid and distilling from potassium bromide. Solutions of halogen in the dry solvents were standardized by titration. Microanalyses, including those for boron, were carried out by Alfred Bernhardt, Mülheim. Ultraviolet spectra were determined using a Unicam S.P. 500 spectrophotometer. Infrared spectra were determined

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(6) M. J. S. Dewar and R. Dietz, *Tetrahedron*, in press.

(7) This possibility was pointed out some time ago by one of us, *cf.* M. J. S. Dewar, *J. Chem. Soc.*, 780 (1946), *The Electronic Theory of Organic Chemistry*, Clarendon Press, Oxford, p. 168 (1949).

(8) R. Fittig and E. Ostermayer, *Ann.*, **166**, 361 (1873).

(9) M. J. S. Dewar and E. W. T. Warford, *J. Chem. Soc.*, 3570 (1956).

(10) M. J. S. Dewar, R. Dietz, V. P. Kubba, and A. R. Lepley, *J. Amer. Chem. Soc.*, *in press.*

using a Grubb-Parsons G.S.2A Double Beam instrument. Melting points are uncorrected.

ω-Chloro-2-aminostyrene. 2-Nitrocinnamic acid gave, on treatment with hypochlorous acid, a 7% yield of ω-chloro-2-nitrostyrene, m.p. 55.5–56.5° (lit.[11] 57.5–58.5°). Reduction with stannous chloride and aqueous-alcoholic hydrogen chloride gave a 61% yield of ω-chloro-2-aminostyrene m.p. 54–55.5° (lit.[11] 55.5–56.5°).

Bis(3-Chloro-2,1-borazaro-2-naphthyl) ether. ω-Chloro-2-aminostyrene (1.16 g., 7.6 mmoles) in methylene chloride (10 ml.) was added slowly to boron trichloride (2 g., 17 mmoles) at −70°. No hydrogen chloride was evolved while the mixture was allowed to warm to room temperature. Removal of solvent and excess of boron trichloride at 20° and 0.5 mm. left a viscous oil, which was dissolved in dry benzene (30 ml.) and heated. Hydrogen chloride (1.5 mmoles) was swept from the apparatus in a stream of dry nitrogen and absorbed in water while the mixture was boiled under reflux for 4 hr. No boric acid could be detected by further titration in the presence of mannitol. The red solution was cooled before ether (50 ml.) and water (20 ml.) were added. The organic layer was washed with hydrochloric acid (2*N*, 2 × 30 ml.) and water (30 ml.), dried (magnesium sulfate), and evaporated to give bis(3-chloro-2,1-borazaro-2-naphthyl) ether (1.26 g., 97%) m.p. 236–239°. Crystallization from benzene petroleum ether (b.p. 80–100°) gave fine needles, m.p. 240–241.5°.

Anal. Calcd. for $C_{16}H_{12}N_2B_2Cl_2O$: C, 56.4; H, 3.6; N, 8.2; B, 6.4; Cl, 20.8. Found: C, 56.5: H, 3.8; N, 8.4; B, 6.6; Cl, 20.6.

2-Methoxy-3-chloro-2,1-borazaronaphthalene. Crystallization of the above ether from methanol gave 2-methoxy-3-chloro-2,1-borazaronaphthalene, m.p. 88–89.5°. Slow but quantitative hydrolysis to the ether took place on storing in air.

Anal. Calcd. for C_9H_9NBOCl: C, 55.9; H, 4.7; N, 7.2; B, 5.6; Cl, 18.3. Found: C, 56.1; H, 4.8; N, 7.4; B, 5.8; Cl, 18.3.

2-Methyl-3-chloro-2,1-borazaronaphthalene. Bis(3-chloro-2,1-borazaro-2-naphthyl) ether (0.5 g., 1.5 mmoles) in an ether slurry (40 ml.) was added to methylmagnesium iodide (7.1 mmoles) in ether (30 ml.) with stirring at room temperature. The mixture was boiled under reflux for 3 hr. before being hydrolyzed with hydrochloric acid (2*N*, 30 ml.), dried (magnesium sulfate) and evaporated to give a light brown solid (0.52 g.). Elution from a column of alumina (100–200 mesh, 5 × 2 in.) with petroleum ether (b.p. 40–60°) gave 2-methyl-3-chloro-2,1-borazaronaphthalene (0.48 g., 90%) m.p. 117–119°. Crystallization from petroleum ether (b.p. 40–60°) raised the melting point to 119–120.5°.

Anal. Calcd. for C_9H_9NBCl. C, 60.9; H, 5.1; N, 7.9; Cl, 20.0. Found: C, 61.1; H, 5.1; N, 7.7; Cl, 19.7.

Halogenation of 2-methyl-2,1-borazaronaphthalene. (a) In *glacial acetic acid.* Chlorine (15 mmoles) in acetic acid (0.43*M*) was added with stirring to 2-methyl-2,1-borazaronaphthalene (2.01 g., 14 mmoles) in acetic acid (50 ml.) at 18° over 1 hr., and the mixture was stirred for a further hour. Water (800 ml.) was added and the mixture was filtered. The solution of the solid in ether (80 ml.) was washed successively with water (50 ml.), hydrochloric acid (2 × 50 ml., 2*N*), and water (50 ml.) before being dried (magnesium sulfate) and evaporated.

The residue (0.92 g.) was separated by chromatography on alumina (2 in. × 6 in. column). Elution with petroleum ether (b.p. 40–60°; 50 ml.) gave 2-methyl-2,1-borazaronaphthalene (0.05 g.). A further 7 l. gave 2-methyl-2-chloro-2,1-borazaronaphthalene (0.62 g., 25%) m.p. and mixed m.p. 119-120.5°. The infrared and ultraviolet spectra and of authentic 2-methyl-3-chloro-2,1-borazaronaphthalene were identical. Subsequent elution with petroleum ether (b.p. 40–60°; 3 l.), ether (7 l.), chloroform (4 l.), and ethanol (7 l.) removed nothing from the column.

The combined aqueous filtrate and washings were made basic with ammonia (sp. gr. 0.880) and extracted with ether (4 × 150 ml.). The ethereal solution was dried (magnesium) and evaporated to give a brown oil (1.46 g.). Extraction with boiling pentane gave ω-chloro-2-aminostyrene (1.41 g., 67%) m.p. 49–51°. Crystallization from pentane raised the melting point and mixed melting point to 50.5–52°. The infrared spectrum was identical with that of authentic ω-chloro-2-aminostyrene.

Similarly, bromination produced *2-methyl-3-bromo-2,1-borazaronaphthalene,* m.p. 128–129.5°.

Anal. Calcd. for C_9H_9NBBr: C, 48.7; H, 4.1; N, 6.3; Br, 36.0; B, 4.9. Found: C, 48.4; H, 4.1; N, 6.5; Br, 36.0; B, 5.3 and *ω-bromo-2-aminostyrene,* m.p. 78.5–79.5°.

Anal. Calcd. for C_8H_8NBr: C, 48.4; H, 4.0; N, 7.1; Br, 40.1. Found: C, 48.6; H, 4.2; N, 6.8; Br, 40.5.

(b) *In carbon tetrachloride.* Chlorine (15 mmole) in carbon tetrachloride (0.5*M*) was added over 1 hr. to 2-methyl-2,1-borazaronaphthalene (1.82 g., 13 mmoles) in carbon tetrachloride (50 ml.). A white precipitate appeared during the addition. Stirring was continued for 1 hr. before the solution was washed with water (70 ml.), hydrochloric acid (2*N*, 50 ml.), and water (50 ml.). The dried (magnesium sulfate) solution was evaporated to leave a black tarry solid. Digestion with ether removed a white solid (0.24 g.) from this which gave *2-methyl-3-chloro-2,1-borazaronaphthalene,* m.p. and mixed m.p. 117.5–119.5 (0.17 g., 8%) when chromatographed.

The combined aqueous washings were made strongly basic with ammonia and extracted with ether (4 × 130 ml.). The fluorescent solution was dried (magnesium sulfate) and evaporated to give nearly pure ω-chloro-2-aminostyrene (1.20 g., 66%), m.p. and mixed m.p. 52.5–54°.

The yields produced under slightly different conditions are summarized (Table I).

Acknowledgment. The work described here was carried out at Queen Mary College, University of London. We wish to thank that University for the award of the William Lincoln Shelley Research Studentship (to R.D.) and Eastman Kodak Ltd. for a gift of crude 2-amino phenethanol.

CHICAGO, ILL.

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[11] G. Kommpa, *Ber.*, **26**, 2969 (1893).