Cl, 25.3) which corresponds to $(C_6H_5O)_3PCl_2$ contaminated with some unknown material. Zhmurova and Kirsanov[6] regarded this material as pure dichlorotriphenoxyphosphorane (1) and reported for it a melting point of 76–78° but gave no elemental analysis or any other physical properties.

Reaction of 2 Mol of Phenol with the Product of the Reaction of Phosphorus Pentachloride with Triphenyl Phosphite. Procedure of Zhmurova and Kirsanov.[6] Phenol (4.5 g, 48.5 mmol) was added at once to the product made from triphenyl phosphite and phosphorus pentachloride as described above (Kirsanov procedure[6]) (6.82 g, 24.2 mmol). The mixture was kept 2 hr at 150° and then was kept 1 hr at 100° (10 mm) and 3 hr at 150° (10 mm). An aliquot was dissolved in methylene chloride; this solution had two ^{31}P nuclei in the proportion of 3.4:1 at $\delta^{31}P$ +22.8 [$(C_6H_5O)_3PCl_2$] and +17.5 ppm (probably triphenyl phosphate). The main portion of the reaction mixture became a solid at 30° and was submitted to elemental analysis (Found: C, 67.6; H, 4.9; Cl, 5.2) which corresponds to a mixture of dichlorotriphenoxyphosphorane and phenol. Zhmurova and Kirsanov[6] assumed that this material was pentaphenoxyphosphorane (2); they gave its melting point as 80–90°, but provided no elemental analysis or other physical properties.

Reaction of Phosphorus Pentachloride with an Excess of Triphenyl Phosphite at 25°. Phosphorus pentachloride was added to an excess of triphenyl phosphite at 25°. The ^{31}P nmr spectrum of this mixture contained four ^{31}P nuclei in addition to that of triphenyl phosphite ($\delta^{31}P$ −127.5 ppm) in the following proportions: 3.0:4.0:2.0:1.0 at $\delta^{31}P$ +23.0, −176.2, −157.5, and +296.5 ppm. There was no PCl_3 in this mixture.

Chlorination of Triphenyl Phosphite. Chlorine was bubbled through a solution of triphenyl phosphite in hexane. A colorless precipitate was formed. This was filtered in the absence of moisture and was dissolved in several solvents for measurement of the ^{31}P nmr shifts. The values are given in the Results section. No suitable crystallization solvent was found for this material. The closest analytical values for $(C_6H_5O)_3PCl_2$ which could be obtained in this type of preparation were: C, 60.8; H, 4.4.

When this material was treated with 2 molar equiv of phenol, no change in the ^{31}P nmr shift was noted.

New Heteroaromatic Compounds. XXX.[1] A Derivative of 10,9-Borathiarophenanthrene[2,3]

Franklin A. Davis[4] and Michael J. S. Dewar

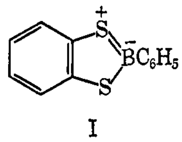
Contribution from the Department of Chemistry, The University of Texas, Austin, Texas 78712. *Received January 19, 1968*

Abstract: Bis(10,9-borathiarophenanthryl) ether has been prepared, this being the first heteroaromatic[5] boron compound containing boron and sulfur in a six-membered aromatic ring. Comparison of its properties with those[4] of the corresponding nitrogen[6] and oxygen[7] compounds shows that the sulfur-containing system is by far the least aromatic.

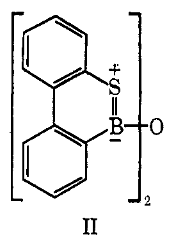
Previous papers of this series[5–7] have described a novel series of heteroaromatic compounds, isoconjugate with "normal" aromatic systems and derived from them by replacing a pair of adjacent carbon atoms by boron and nitrogen, or boron and oxygen.

In part II,[8] a compound (I) was described in which two carbon atoms of a typical aromatic system, *i.e.*, thianaphthalene, were likewise replaced by boron and sulfur; as yet, however, no compounds have yet been reported in which boron and sulfur form part of a six-membered aromatic ring. We have now prepared a compound of this type, bis(10,9-borathiaro-10-phenanthryl) ether (II) and examined its properties, with a view to establishing its aromaticity relative to that of the isoconjugate nitrogen[6] (III) and oxygen[7] (IV) derivatives.

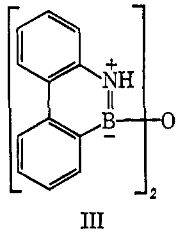
The synthesis of II followed the same general procedure used[6,7] in the preparation of III or IV. 2-Mercaptobiphenyl[9] (V) reacted with an excess of boron trichloride to give, presumably, the dichloride VI. This on treatment with aluminum chloride, followed by moist ether, yielded an oil which solidified when washed with petroleum ether (bp 30–60°). Sublimation of the solid gave a white powder, mp 170–171°, identified as II. Attempts to isolate the intermediate chloride VII failed since it was extremely sensitive to hydrolysis.



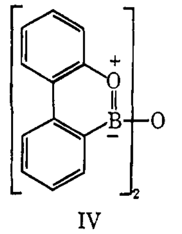
I



II



III



IV

The petroleum ether used to wash II contained two other compounds, identified as dibenzothiophene (VIII) and tris(2′-mercapto-2-biphenyl)boroxine (IX). The structures of II and IX were established by ele-

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[1] Part XXIX: M. J. S. Dewar, R. Jones, and R. H. Logan, Jr., *J. Am. Chem. Soc.*, in press.

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

[3] Presented in part at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967.

[4] Robert A. Welch Postdoctoral Fellow.

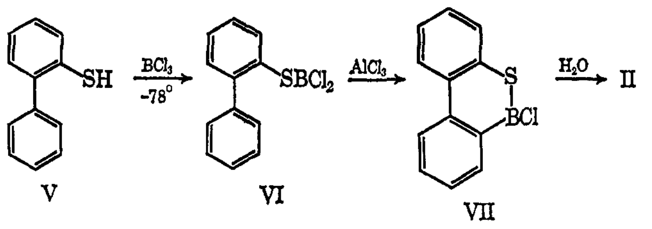
[5] See M. J. S. Dewar, *Progr. Boron Chem.*, **1**, 235 (1964); and R. F. Gould, Ed., Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D. C., 1964, p 227.

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

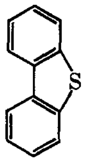
[7] M. J. S. Dewar and R. Dietz, *ibid*, 1344 (1960).

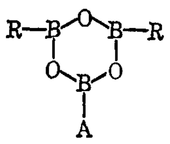
[8] M. J. S. Dewar, V. P. Kubba, and R. Pettit, *ibid.*, 3076 (1958).

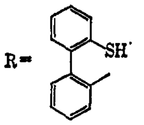
[9] D. D. Emrich and W. E. Truce, *J. Org. Chem.*, **25**, 1103 (1960).



mental analysis and by their infrared, proton nmr, and mass spectra.


VIII


IX



The infrared spectrum of II showed strong absorption at 1325 and 1265 K. Such absorption has been attributed to the symmetrical stretching modes of the B–O–B group, respectively.[10] The weak absorption at 935 cm^{-1} probably corresponds to B–S stretching;[11] this bond was absent in the spectrum of IX. The molecular weight of II was indicated by a parent peak (*m*/*e* 406) in the mass spectrum. Attempts to determine the molecular weights of II or IX by the Rast method or vapor phase osmometry proved unsatisfactory, since both compounds are apparently very susceptible to hydrolytic cleavage of the B–O–B link. Both methods with either compound gave values in the region 200–210. Such a molecular weight would correspond to a structure in which at least one B–O–H group was present; no hydroxyl absorption was observed in the infrared spectra of II or IX.

The proton nmr spectra of II and IX also supported the assigned structures. It is known that the protons in the 4,5 positions of phenanthrene absorb downfield by about 1 ppm relative to the other protons; this difference has been attributed to magnetic deshielding[12] and/or steric crowding of protons in the 4,5 positions.[13] The effect can in any case be attributed to the presence of a coplanar biphenyl structure, for no such difference is observed between the *ortho* protons and the remaining protons in biphenyl itself, a compound which is believed to be noncoplanar in solution or the gas phase,[14] while smaller differences are observed in 9,10-dihydrophenanthrene where the rings are not quite coplanar, and in dibenzothiophene (VIII) where the 4,5 positions are further apart than they are in phenanthrene. Table I lists data for a number of relevant compounds; note that the borazarophenanthrene derivative III and the boroxarophenanthrene derivative IV also show the effect. Now the proton nmr spectrum of II consists of a multiplet at δ 7.52 and a doublet at δ 8.42, with intensities in a ratio 3:1; the pattern is exactly analogous (Table I) to that observed for phenanthrene III and IV. II must therefore contain a bridge across two *ortho* positions of the biphenyl moiety; consequently, it must be a derivative of 10,9-borathiarophenanthrene. Conversely the proton nmr spectrum of IX showed only a single band in the aromatic region; IX must therefore have an open biphenyl structure.

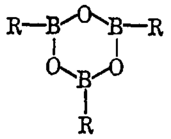
Table I. Differences in Chemical Shift (Hz at 60 MHz) between the 4,5 Protons and Other Protons in Compounds Analogous to Phenanthrene

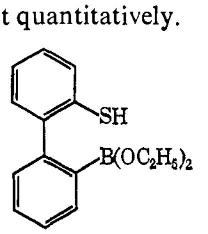
Compound	Chemical shifts, δ[a]	Difference, Hz
Phenanthrene[b]	8.0, 7.1	55
Biphenyl[c]	7.1	0
VIII	7.9, 7.25	39
9,10-Dihydrophenanthrene[d]	7.7, 7.25	27
III	8.1, 7.1	60
IV	8.2, 7.4[e]	48
II	8.4, 7.5	54
IX	7.4	0

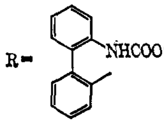
[a] Aromatic protons in carbon disulfide, unless otherwise stated. [b] C. Reid, *J. Am. Chem. Soc.*, **78**, 3225 (1956). [c] Varian Associates, Nmr Catalog, Palo Alto, Calif., 1963. [d] Sadtler Standard Spectra, "Nuclear Magnetic Resonances Spectra," Sadtler Research Laboratories, Philadelphia, Pa., 1965. [e] In chloroform-*d*.

The infrared spectrum of IX showed weak absorption at 2560 K (S–H stretching[15]), strong absorption at 690 K characteristic of a boroxine ring,[16,17] and bands at 1076, 1048, and 1010 K characteristic of triphenylboroxine.[16] None of these bands were present in the spectrum of II. The proton nmr spectrum showed a single multiplet in the aromatic region (δ 7.1) and a singlet at δ 2.95 (SH), with intensities in the ratio 8:1. The ultraviolet spectrum of IX in ethanol was similar to that of tris(2′-carbethoxyamido-2-biphenylyl)boroxine (X),[18] being likewise typical of a hindered biphenyl (Figure 1).

The structure of VIII was established by comparison with an authentic sample. It was probably formed by oxidative ring closure from V in the presence of aluminum chloride; for under the conditions used to convert VI to VIII, V gave VIII almost quantitatively.


X


XI



The borathiarophenanthrene II proved extremely sensitive to hydroxylic solvents. Treatment with cold

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(10) W. Gerrard, "The Organic Chemistry of Boron," Academic Press Inc., New York, N. Y., 1961.

(11) See R. H. Cragg, M. F. Lappert, and B. P. Tilley, *J. Chem. Soc., A*, 947 (1967).

(12) J. A. Pople, *J. Chem. Phys.*, **24**, 1111 (1956).

(13) C. Reid, *J. Mol. Spectry.*, **1**, 18 (1957).

(14) O. Bastiansen, *Acta Chem. Scand.*, 3, 408 (1949).

(15) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958.

(16) P. W. Abrey, R. F. Lappert, and H. Pyson, *J. Chem. Soc.*, 1931 (1961).

(17) H. R. Snyder, M. S. Konecky, and W. J. Lennarz, *J. Am. Chem. Soc.*, 80, 3611 (1958).

(18) M. J. S. Dewar and P. M. Matilis, *Tetrahedron*, **15**, 35 (1961).

Table II. ^{11}B Nmr Spectra of Heteroaromatic Boron Compounds

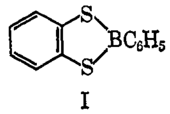
Compound	Solvent	Chemical shift[a]	Line width,[b] Hz
Bis(10,9-borathiaro-10-phenanthryl) ether (II)	CS_2	−42.9	387
	EtOH	−28.5	315
Bis(10,9-borazaro-10-phenanthryl) ether (III)	CS_2	−29.5[19]	266
	EtOH	−29.3[19]	221
	5% KOH–EtOH	−43.9[20]	2500
Bis(10,9-boroxaro-10-phenanthryl) ether (IV)	EtOH	−28.8	233
	5% KOH–EtOH	−5.5	162
Tris(2′-mercapto-2-biphenylyl)boroxine (IX)	CS_2	−31.9	308
	EtOH	−28.8	315
	5% KOH–EtOH	−1.6	80
2-Phenyl-1,3,2-benzodithiaborole	CS_2	−59.3	135
2-Phenyl-1,3,2-benzodiazaborole (XII)	CH_3CN	−27.7	115
2-Phenyl-1,3,2-benzodioxaborole (XIII)	CS_2	−31.9	111
Boric acid	5% KOH–EtOH	−1.6	80

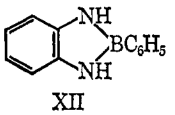
[a] Relative (parts per million) to diethyl ether–boron trifluoride complex. [b] Measured at half-height.

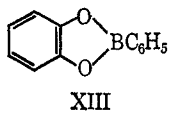
ethanol converted it immediately to the boronic ester XI, the ultraviolet spectrum of which (Figure 1) showed end absorption characteristic of a hindered biphenyl. The boroxine IX seemed on the other hand stable to ethanolysis since its ultraviolet spectrum in ethanol, while also characteristic of a hindered biphenyl, differed from that of II. Attempts to regenerate II by heating XI gave only the boroxine IX. The ultraviolet spectrum of II in decalin, on the other hand, showed some structure, in particular a weak band at 325 nm. The corresponding nitrogen (III) and oxygen (IV) compounds show strong characteristic absorption in this region, suggesting at first sight that the central ring in II must be less aromatic than that in III or IV; however, although stringent precautions were taken to exclude moisture, we cannot be certain that II may not have undergone hydrolysis, given that it is so sensitive and given that only minute traces of water would be required to destroy the very dilute solutions used for ultraviolet spectrometry.

The sensitivity of II to hydrolysis is in marked contrast to the corresponding nitrogen analog III, which is unaffected[5] (apart from hydrolysis of the ether linkage) by boiling concentrated hydrochloric acid or strong alkali. This difference can easily be understood if the exceptional stability of III is due to mesomeric stabilization[5] of the central ring; for, since sulfur is much less effective at forming π bonds than nitrogen or oxygen, any such stabilization should be much less in the case of II than III.

Further evidence for this interpretation was provided by the ^{11}B nmr spectrum of II. Recent work[19] has shown that the ^{11}B chemical shift in compounds of this type provides a useful criterion of the degree of π bonding to boron, and also of the mode of salt formation by compounds containing the grouping B–O–H.[20] Table II compares the behavior of II with that of its nitrogen (III) and oxygen (IV) analogs; for reference we also measured the ^{11}B nmr spectrum of the dithiaborole I[8] for comparison with the spectra[19] of its nitrogen (XII)[8] and oxygen (XIII)[8] analogs (Table II).


I


XII


XIII

It will be seen that the sulfur compounds I and II absorb far downfield in comparison with the nitrogen analogs III and XII, or the oxygen analogs IV and XIII. This indicates[19] very clearly that dative π bonding to boron must be very much less important in I and II than in the analogs containing nitrogen or oxygen, in agreement with our interpretation of the much greater chemical reactivity of II.

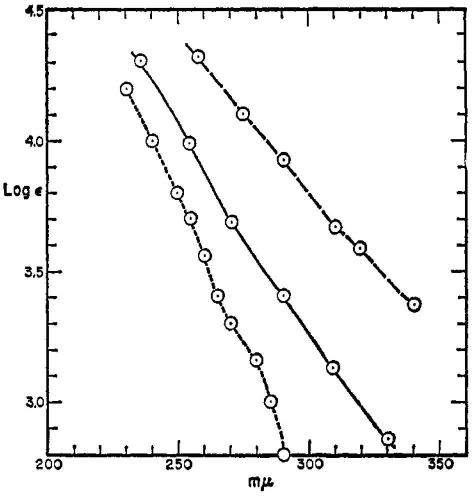


Figure 1. Ultraviolet spectra of IX (– –⊙– –), X (—⊙—), and XI (- -⊙- -).

Note also the large upfield shift shown by II in ethanol in comparison with carbon disulfide; this of course is in agreement with the chemical evidence that indicates solvolytic fission of the central ring of II on solution in ethanol. The observed absorption (at −28.5 ppm) is very close to that observed for diethyl phenylboronate (−28.6 ppm[19]). The central rings in III and IV are stable to ethanol,[21] this difference from II being due to the fact that π bonding to boron from an adjacent nitrogen or oxygen must be much more efficient than from an adjacent sulfur atom.

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(19) F. A. Davis, M. J. S. Dewar, and R. Jones, *J. Am. Chem. Soc.*, in press.

(20) M. J. S. Dewar and R. Jones, *ibid.*, **89**, 2408 (1967).

(21) The ultraviolet spectra of III and IV in ethanol show[6,7] strong absorption in the 320-nm region, characteristic of the borazaro- and boroxarophenanthrene rings, and absent in derivatives of 2-amino- or 2-hydroxybiphenyl.

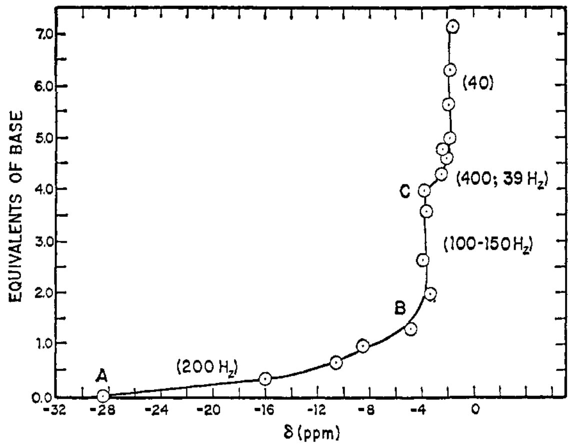
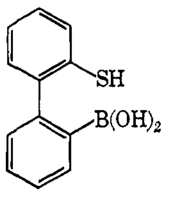


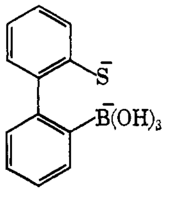
Figure 2. Plot of the shift (δ) in parts per million of the ^{11}B nmr resonance of IX in ethanol against equivalents of added potassium hydroxide. Line widths (hertz) are given in parentheses.

One would expect IV in turn to be less aromatic than III, since oxygen, being much more electronegative than nitrogen, should be correspondingly less efficient at forming dative π bonds to boron. It is true that 10-phenyl-10,9-boroxanphenanthrene undergoes oxidative cleavage of the phenyl–boron bond with great ease, unlike the very stable nitrogen analog; however, spectroscopic evidence had suggested[7] that IV, like III, behaves as a protic acid and so must possess a highly aromatic central ring. We have now found that this is not the case; for solution of IV in alkali leads (Table II) to a large upfield shift of the ^{11}B resonance, together with line narrowing, behavior indicating unambiguously that IV acts as a Lewis acid, rather than a protic acid, to hydroxide ion. Further investigation[22] has confirmed this conclusion and has shown that the conclusion in the original paper[7] was based on a misinterpretation of the ultraviolet spectroscopic data.

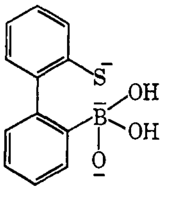
Attempts to study the ^{11}B nmr spectrum of the boroxine IX in alkali led to an unexpected result. On adding alkali to an ethanol solution of IX, a large upfield shift was observed (Table II), as would be expected if hydrolysis had taken place to the corresponding arylboronic acid, for arylboronic acids behave as Lewis acids to base.[20] Further investigation showed, however, that the observed spectrum could not be that of 2′-mercapto-2-biphenylboronic acid (XIV) since the ^{11}B resonance appeared too far upfield, and since the line width was much less than that observed[20] for solutions of arylboronic acids in alkali. The observed spectrum proved to be identical with that exhibited by boric acid under the same conditions (Table II), and on examining the alkaline solution of IX we found that it indeed contained boric acid, together with dibenzothiophene (VIII) which was isolated in more than 60% yield.



XIV



XV

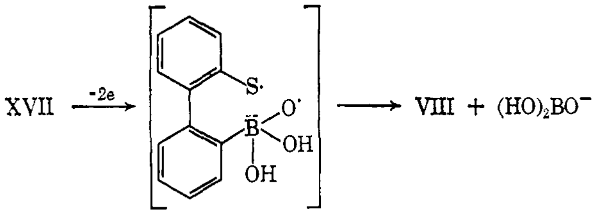


XVI

The formation of VIII and boric acid from IX must involve an oxidation; the oxidizing agent was shown to be air by repeating the reaction with carefully degassed solvents in an inert atmosphere when no VIII was formed. Further information concerning the mechanism of the reaction was provided by "nmr titration" of IX, the ^{11}B nmr spectrum in ethanol being measured as a function of added potassium hydroxide. Figure 2 shows the results.

Evidently the section AB of the curve corresponds to neutralization of the boronic acid and thiol functions of IX to form XV, 2 equiv of base being required. Since the main change occurred during addition of the first equivalent, one can conclude that the boronic acid function is the more acidic. There was also a decrease in line width from 200 Hz at A to *ca.* 125 Hz at B, as would be expected[20] in passing from IX to XV. Further addition of base up to point C (4 equiv) produced no further change in the ^{11}B nmr spectrum; up to this point, acidification of the solution regenerated IX. After C, however, addition of still more base produced a further upfield shift in the ^{11}B resonance; the line width first increased to 400 Hz, then decreased, the final spectrum being identical with that of the ion $B(OH)_4^-$. Acidification of the solution no longer gave any unchanged IX, while dibenzothiophene (VIII) could be isolated in good yield.

Clearly the conversion of IX to VIII must involve attack by yet a third molecule of base, presumably giving the trianion XVI; this would be expected[20] to show a broader ^{11}B resonance than XV since the field around boron is less symmetrical. Conversion of XVI to VIII by oxygen presumably involves an over-all two-electron transfer to yield ultimately hydrogen peroxide; it is true that no hydrogen peroxide was detected in the reaction product, but then hydrogen peroxide would not only be unstable under the alkaline conditions used but also would presumably itself act as an oxidizing agent to XI, yielding VIII and water. The over-all reaction can then be written formally as follows.



Probably, however, the oxidation takes place in stages, by two separate one-electron transfers, rather than by a single two-electron process.

One final piece of evidence concerning the relative aromaticities of II, III, and IV is provided by their mass spectra. All three compounds showed prominent parent peaks, as would be expected if they are aromatic. However, in the case of III and IV, the base peaks corresponded to the fragments formed by single ether cleavage, the phenanthrene-like ring system remaining intact, whereas the corresponding peaks in the case of II were weak. The base peak in the case of II (*m/e* 184) corresponded to the value expected for dibenzothiophene (VIII), implying that in this case the central ring fragments with loss of BO. This result again implies a

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[22] F. A. Davis and M. J. S. Dewar, submitted for publication.

much lower degree of aromaticity for the central ring of II than for the central rings of III or IV.

Experimental Section

^{11}B nmr spectra were measured with a Varian DP-60 spectrometer using procedures described[20] previously. Melting points are uncorrected. Solvents were purified by standard methods.

Bis(10,9-borathiaro-10-phenanthryl) Ether (II). A solution of 2-mercaptobiphenyl[9] (3.0 g, 0.016 mol) in dry methylene chloride (50 ml) was added dropwise to a stirred solution of boron trichloride (3.7 g, 0.032 mol) in dry methylene chloride (100 ml) under nitrogen at −78°. After 3 hr at −78°, followed by 6 hr at 0°, the solution was evaporated under vacuum, the residue dissolved in dry benzene (100 ml), aluminum chloride (0.1 g) added, and the mixture left overnight at room temperature and then filtered. Evaporation under vacuum, treatment with moist ether followed by filtration (to remove boric acid), and evaporation gave a yellow oil which solidified on treatment with petroleum ether (bp 30–60°). Fractional sublimation gave (at 190° (0.03 mm)) II as a white powder, mp 171–172°.

Anal. Calcd for $C_{24}H_{16}B_2OS_2$: C, 70.9; H, 4.0; B, 5.4; S, 15.7; mol wt, 406. Found: C, 70.8; H, 4.1; B, 5.4; S, 15.6; mol wt (Rast), 203 (see text).

The proton nmr spectrum in carbon disulfide consisted of multiplets at δ 7.5 and 8.4 (integrated absorptions in the ratio 3:1). The infrared spectrum (KBr disk) showed bands at 1610 (m), 1580 (w), 1480 (w), 1445 (m), 1360 (s), 1335 (s), 1270 (m), 1100 (w), 935 (w), 755 (ms), 750 (s), 735 (m), and 710 (w) K. The ultraviolet spectrum in decalin showed bands at 322 nm (log ϵ 3.14), 309 (3.18), 278 (3.63). The mass spectrum showed peaks at *m/e* 408 (11.7%), 407 (18.7%), 406 (parent ion, 78%), 405 (67%), 212 (27%), 211 (14%), 186 (30%), 185 (20%), 184 (base ion, 100%), 183 (10%), 152 (17%), and 139 (18%).

Dibenzothiophene (VIII). Evaporation of the petroleum ether used to wash II gave a white solid, from which dibenzothiophene (X) (0.6 g, 33%), mp and mmp 98–99° (lit.[23] 99°), was isolated by sublimation at 80° (0.03 mm). The uv and ir spectra were identical with those of an authentic sample (Aldrich Chemical Co.).

Tris(2′-mercapto-2-biphenylyl)boroxine (IX). Sublimation of the residue from VIII at 150–160° (0.03 mm) gave IX (0.89 g, 37%) which crystallized from petroleum ether (bp 30–60°) in colorless plates, mp 155–156°.

Anal. Calcd for $C_{36}H_{27}B_3O_3S$: C, 68.0; H, 4.3; B, 5.2; S, 15.1; mol wt, 636. Found: C, 68.1; H, 4.4; B, 5.0; S, 15.0; mol wt (Rast), 219 (see text).

The proton nmr spectrum in carbon disulfide showed multiplets at δ 7.1 and 2.95, with integrated absorptions in the ratio 8:1. The infrared spectrum (KBr disk) showed bands at 2560 (w), 1600 (mw), 1560 (mw), 1470 (m), 1450 (m), 1360 (s), 1335 (s), 1300 (m), 1274 (w), 1255 (w), 1240 (w), 1076 (w), 1010 (w), 755 (s), and 695 (s) K.

Conversion of III to IX. Solution of III in ethanol, evaporation to dryness, and sublimation of the residue gave IX, identical with an authentic specimen.

Conversion of III or IX to VIII. A solution of IX (0.1 g) in ethanolic potassium hydroxide (2.0 ml of 5%) was left overnight when VIII (0.06 g) had crystallized. The total recovery ranged from 60 to 70%. When the reaction was repeated with degassed solvents under oxygen-free nitrogen, no VIII was formed.

Properties of III. The proton nmr spectrum of III[5] in carbon disulfide showed multiplets at δ 8.1 and 7.1, ratio of integrated absorptions 3:6. The mass spectrum showed peaks at *m/e* 374 (24.5%), 373 (5.5%), 372 (parent ion, 74%), 371 (42%), 370 (16%), 195 (23%), 194 (base ion, 100%), 192 (13%), 177 (15%), 176 (30%), 175 (15%), 166 (17%), 151 (12%), 150 (15%), 149 (15%), 140 (13%), 138 (12%), 114 (16%), 97 (22%), and 96 (15%).

Properties of IV. The proton nmr spectrum of IV[6] in chloroform-*d* consisted of multiplets at δ 8.2 and 7.4, ratio of integrated intensities 1:3. The mass spectrum showed peaks at *m/e* 375 (8%), 374 (parent ion, 25%), 373 (15%), 196 (17%), 195 (base ion, 100%), 194 (25%), 166 (12%), 151 (32%), 150 (23%), 149 (13%), and 140 (15%).

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(23) H. Gilman and A. L. Jacoby, *J. Org. Chem.*, **3**, 111 (1938).

Nitrogen Ylides. IV. The Role of the Methyl Hydrogen Atoms in the Decomposition of Tetramethylammonium Alkoxides[1]

W. Kenneth Musker and Rex R. Stevens

Contribution from the Department of Chemistry, University of California, Davis, California 95616. *Received July 31, 1967*

Abstract: It has generally been assumed that the demethylation of the tetramethylammonium ion by alkoxides to give methyl ethers proceeds by a bimolecular SN2 mechanism. Although proton abstraction from the tetramethylammonium ion by strong bases to give a nitrogen ylide is a well-known process, this process has never been observed in these demethylation reactions. In this study of the decomposition of various tetramethylammonium alkoxides some proton abstraction to give alcohol is always observed, but the ratio of ether to alcohol remains constant (~4:1), regardless of the steric requirement of alkoxide. By studying the decomposition of tetramethyl-1,1,1-d_3-ammonium methoxide, the dimethyl ether product was found to consist of a mixture of CH_3OCH_3, CH_2DOCH_3, CHD_2OCH_3, and CD_3OCH_3. The extent of hydrogen scrambling in the ether is greater at low temperature (60°) than at high temperature (200°) suggesting that the precursor of the ether is an ylide which rearranges *via* intramolecular hydrogen exchange. The ylide may then react with methanol by a methylene insertion into the O–H bond to give ether. A discussion of this insertion reaction is presented.

Tetramethylammonium salts generally decompose thermally to give trimethylamine and the corresponding methylated anion. Because there is a high yield of the methylated products and a simple stoichiometry,[2] most of these reactions are reported as proceeding by the nucleophilic attack of the anion on the carbon atom of one of the methyl groups in a simple bimolecular process.[3,4] However, it is known that when a strongly basic reagent, such as potassium amide[5a] or phenyllithium,[5b] is treated with the tetramethylam-

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(2) A. T. Lawson and N. Collie, *J. Chem. Soc.*, **53**, 624 (1888).

(3) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 308.

(4) J. Tanaka, J. E. Dunning, and J. C. Carter, *J. Org. Chem.*, **31**, 3431 (1966).