gas chromatography column as the oxazoline obtained by thermolysis of ethyl azidoformate in tetramethylallene.

Photolysis of Ethyl Azidoformate in 1,1-Dimethylallene (XXIV). A stirred solution of 1,1-dimethylallene (XXIV, 34.0 g, 0.50 mol) and ethyl azidoformate (5.60 g, 0.05 mol) in dichloromethane (500 ml) was irradiated at 0°. After the dichloromethane and 1,1-dimethylallene had been removed, the residue was distilled to yield 2-ethoxy-5,5-dimethyl-4-methylene-2-oxazoline (XXV, 3.7 g, 47%), bp 46–47° (2 mm). Analytical and spectral samples were collected from a Carbowax 20M on Chromsorb P45/60 preparative gas chromatography column at 170.

Anal. Calcd for $C_8H_{13}O_2N$: C, 61.91; H, 8.44; N, 9.03. Found: C, 61.83; H, 8.49; N, 9.03.

Acknowledgment. Support of this work by the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. The authors wish to thank Don T. Dix of The Ohio State University and Thomas Page of the Battelle Memorial Institute for their help in the various nmr problems of this research.

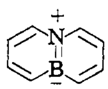
New Heteroaromatic Compounds. XXVIII.[1] Preparation and Properties of 10,9-Borazaronaphthalene[2]

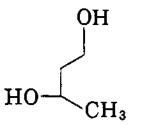
Michael J. S. Dewar and Richard Jones[3]

Contribution from the Department of Chemistry, The University of Texas, Austin, Texas 78712. *Received November 2, 1967*

Abstract: The synthesis of 10,9-borazaronaphthalene (I) has been greatly improved and the intermediates have been characterized. The proton nmr spectrum of I has been completely analyzed and its other properties have been studied; I is isomorphous with the isoelectronic naphthalene. Deuteration and bromination of I lead to preferential attack in the 4(5) position as expected theoretically.

Previous papers of this series[1,4] have described the preparation and properties of a novel series of heteroaromatic compounds, isoelectronic with normal aromatic systems and derived from them by replacement of pairs of adjacent carbon atoms by boron and nitrogen. A comparison of such related aromatic systems present san amusing theoretical problem; however, the comparison is usually complicated by the presence of substituents, since the parent boron-containing compounds would contain the reactive grouping >BH.[5] For this reason 10,9-borazaronaphthalene (I)[6] is of especial interest since the boron atom in it is linked to three atoms other than hydrogen, being at the bridgehead of two fused aromatic rings.


I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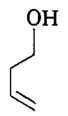
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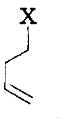
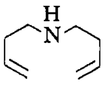
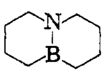

IVa, X = Cl
b, X = Br


V


VI

Recently I was prepared[6] in our laboratories by dehydration of 1,3-dihydroxybutane (II) to 4-hydroxy-1-butene (III), conversion of this *via* the chloride (IVa) into di-3-butenylamine (V), hydroboration to 9-aza-10-boradecalin (VI), and dehydrogenation. However, although sufficient material was obtained in this way for its physical properties to be determined and its nmr spectrum measured, the synthesis in its original form was impracticable as a method for preparing I in any quantity. Not only was the over-all yield extremely low but it was not even reproducible, the two final steps being particularly unsatisfactory in this respect. We have now reexamined this route in some detail and effected major improvements in it. While the over-all yield of I from II is still low (0.2%), it is now reproducible, and, in view of the ready availability of II, this now constitutes a practicable procedure for making I in reasonable amounts.

Synthesis of 10,9-Borazaronaphthalene (I)

It soon becomes apparent that much of the trouble lay in the presence of gross impurities in the amine V. These arise partly in the dehydration of II to III, and partly in the conversion of III to V *via* IVa which proceeds in poor over-all yield. We found that a much better yield of amine could be obtained *via* the bromide IVb than *via* IVa, and that most of the impurities in it could be removed by careful fractional distillation through a Teflon spinning-band column.

None of the intermediates in these stages has ever been properly characterized, and glpc showed them to be complex mixtures; even the structure of the key intermediate V had never been established.[7] We there-

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[1] Part XXVII: F. A. Davis, M. J. S. Dewar, and R. Jones, *J. Am. Chem. Soc.*, 90, 706 (1968).

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

[3] Robert A. Welch Postdoctoral Fellow.

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

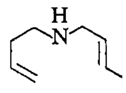
[5] It is true that the parent borazaro compounds are much less reactive than normal boron hydrides; we have for example found that they do not reduce carbonyl derivatives. However, they are easily oxidized by air and react readily with acids or bases.

[6] M. J. S. Dewar, G. J. Gleicher, and B. P. Robinson, *J. Am. Chem. Soc.*, 86, 5098 (1964).

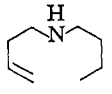
[7] W. Reppe, *Ann.*, 596, 80 (1955), claimed the preparation of V as a by-product from the reaction of 1,4-butenediol with ammonia over

fore thought it advisable to examine the amine in some detail.

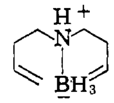
The crude amine, prior to distillation through the spinning-band column, was separated by glpc into a main constituent A, together with smaller amounts of two other amines, B and C. A was shown to be V by its mass spectrum, which displayed a molecular peak at *m/e* 125, and by its nmr spectrum, which indicated the presence of six olefinic protons. The two impurities were likewise shown to be 3-butenyl-*trans*-2-butenylamine (VII), and 3-butenylbutylamine (VIII).



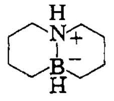
VII



VIII



IX

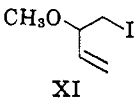


X

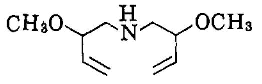
In the original synthesis,[6] V was converted to VI by treatment with trimethylamineborane; we found that a greatly improved yield (60%) was obtained by treating purified V with a 25% excess of diborane at −10°, followed by heating. Only the borane adduct IX is formed at −10°, for, if the solution is submitted to glpc at this stage, no trace of VI is observed. On heating, an intermediate was first formed which could be isolated by glpc and which was still a boron hydride, for its ir spectrum showed the presence of BH, and addition of water led to evolution of hydrogen. This was probably the dihydro derivative X. After prolonged heating, the solution contained only VI, the structure of which was established by elemental analysis and mass spectrometry, and by its nmr spectrum (see below).

The dehydrogenation of VI to I was carried out in 25–30% yield by heating in an autoclave a solution of VI in hexene-1 or octene-1 as hydrogen acceptor, with palladized charcoal as catalyst, for 24 hr at 300°. The product was tested for I by glpc; occasionally the reaction failed, but in these cases a 25–35% yield of I could still be obtained by adding more catalyst and repeating the reaction. The structure of I was indicated by elemental analysis and mass spectrometry, and by its nmr spectrum (see below).

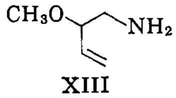
Since attempts to improve the yield in the last step, by altering the conditions, catalyst, or hydrogen acceptor, failed, we tried to prepare an analog of VI with methoxy groups that might facilitate its conversion to I. Butadiene reacted with iodine in methanol to form a product which Petrov[8] formulated as 4-iodo-3-methoxy-1-butene (XI), and with ammonia this was converted to bis(2-methoxy-3-butenyl)amine (XXIa). The primary amine XIII was obtained as a by-product.



XI



XIIa, R = H
b, R = COPh



XIII

Unfortunately, XXIa failed to undergo hydroboration, under a wide variety of conditions. This failure led us to suspect the structure assigned to XI; however, the nmr spectrum of XII confirmed its structure and also helped in interpreting the structures of the amines V, VII, and VIII.

Structures and Nmr Spectra of V, VII, VIII, and XIIa

a. XIIa. The mass spectrum of XIIa showed a parent peak at *m/e* 185, together with a stronger peak at *m/e* 186 (XIIa + H$^+$). The nmr spectrum of XIIa showed an ABX multiplet at δ 4.9–6.05, indicating the presence of a vinyl group, a quartet at δ 3.62, corresponding to the tertiary hydrogen (split by the adjacent methylene group into a triplet, and again by the adjacent vinyl proton, both coupling constants being 5.5 Hz), a doublet at δ 2.57 (J = 5.5 Hz) corresponding to the methylene group, a sharp singlet (methoxy) at δ 3.24, and a rather broad singlet at δ 1.53 (NH). The integrated absorptions were in expected ratios (3:1:2:3:1). The only surprising feature of the spectrum is the appearance of the NH signal so far upfield; however, the assignment was confirmed by its disappearance when the spectrum was measured in acidic deuterium oxide, and by its absence in the spectrum of the benzoyl derivative XXIb. These results are entirely consistent with the formulation of this amine as XIIa and inconsistent with any isomeric structure.

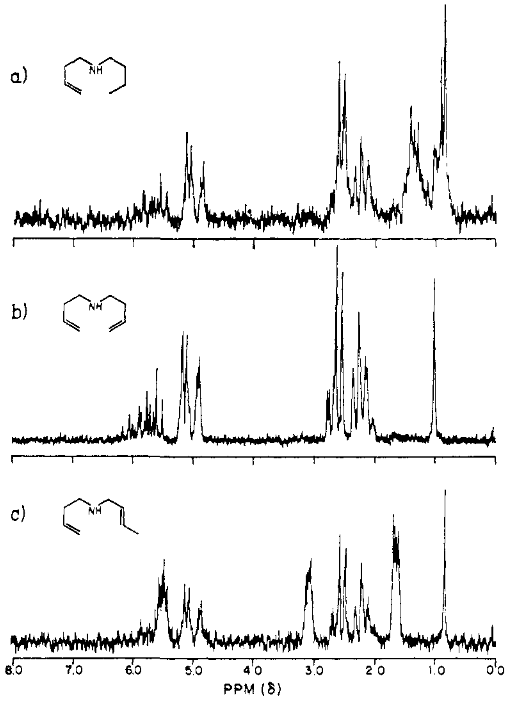


Figure 1. Nmr spectra of (a) VIII; (b) V; (c) VII.

b. V. The mass spectrum of V showed a strong parent peak at *m/e* 125. The nmr spectrum (Figure 1b) showed absorption in the olefinic and aliphatic regions in the ratio 6:9; this indicates the presence of six olefinic protons and so shows the compound to have two vinyl groups. The quartet at δ 2.21 can be assigned to a methylene group adjacent to the vinyl group and coupled both to the vinylic proton and to another methylene, both coupling constants being equal (J = 5.5 Hz); this agrees with the assignment of the signal for the tertiary hydrogen in XIIa (see above). The sextet at δ 2.63 corresponds to the methylene group adjacent to nitrogen, this being split into a triplet (J = 5.5 Hz) by the adjacent methylene, and further split (J = 2 Hz) by the tertiary proton. The signal for the NH proton again appears as a singlet at unexpectedly

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alumina at 300°; however, the positions of the double bonds were not determined.

[8] A. A. Petrov, *Zh. Obshch. Khim.*, 19, 1046 (1949).

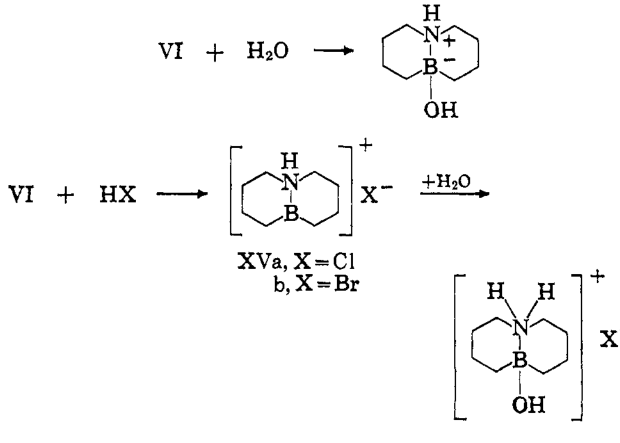
high field (δ 1.02); this assignment was confirmed by measuring the spectrum in formic acid when the signal at δ 1.02 disappeared. Further support for the assignments indicated above, and so for the structure of V, came from the differences between the chemical shifts of the protons of V in carbon tetrachloride, and in formic acid. The signal attributed to the methylene group adjacent to nitrogen shifted downfield by 40 Hz, while that for the other methylene shifted by only 21 Hz, while the olefinic absorption remained more or less unchanged. This indicates the relative distances of the protons from the charged $>NH_2^+$ group in the salt formed from V in formic acid. The ir spectrum showed bands at 3.31 (NH stretch), 3.09 (CH stretch), and 1.65 kK (C=C stretch).

c. VIII. The mass spectrum at VIII showed a parent peak at *m/e* 127, corresponding to (V + 2H). The nmr spectra (Figure 1a) showed absorption identical with that for V, plus additional signals: this indicated the presence of a 3-butenylamino grouping, the additional signals corresponded to two methylene groups (complex multiplet of δ 1.1–1.6, integrated absorption equivalent to four protons) and a methyl group (triplet at δ 0.92). The ir spectrum showed absorption at 3.09 and 1.65 kK, similar to but weaker than those observed for V. These results, together with the method of synthesis, establish the structure of VIII unequivocally.

d. VII. The mass spectra of VII showed a parent peak at *m/e* 125, indicating that it is an isomer of V; this was confirmed by elemental analysis. The nmr spectrum (Figure 1c) showed absorption corresponding to olefinic and paraffinic protons in the ratio 5:10; the spectrum showed bands in all the same positions as that of V, confirming the presence of a 3-butenyl group. The remaining olefinic absorption (two protons) appeared as a complex multiplet. A second complex multiplet (two protons, δ 3.1) is in the correct position and of the correct intensity to correspond to a methylene group adjacent to both nitrogen and a double bond. The last absorption (three protons) was a doublet of doublets at δ 1.7, consistent with a methyl group adjacent to —CH=CH—. These results establish that the compound was a 2-butenyl-3-butenylamine; several lines of evidence show that the 2-butenyl group had a *trans* configuration. First, if one subtracts from the olefinic absorption the contribution due to the vinyl group of 3-butenyl (*cf.* Figure 1b), one is left with a multiplet which is almost identical in form with that observed for *trans*-crotyl alcohol, but quite different from that for the *cis* isomer.[9] Secondly, the ir spectrum showed strong absorption at 970 K which is absent from the spectra of V, VIII, or XII, and is characteristic of CH deformations in *trans*-disubstituted ethylenes.[10] Thirdly, the amine must have arisen from crotyl alcohol, present as an impurity in III; since III was prepared from II under acidic conditions, any crotyl alcohol formed should have been present mainly as its most stable geometrical isomer, *i.e.*, *trans* rather than *cis*.

9-Aza-10-boradecalin (VI)

The structure of VI was indicated by elemental analysis, by its mass spectrum which showed a parent peak at *m/e* 137, together with a base peak at *m/e* 136 (corresponding presumably to loss of hydrogen α to nitrogen, a phenomenon commonly observed in tertiary amines), and by its nmr spectrum which consisted of three multiplets centered at δ 2.8, 1.6, and 0.7 with integrated absorptions in the ratio 1:2:1; these are in the positions expected for methylene adjacent to nitrogen, methylene in a hydrocarbon chain, and methylene adjacent to boron, respectively. The compound was unstable in air, being converted to a crystalline solid which analyzed for (VI + H_2O), and whose mass spectrum showed strong peaks corresponding to VI and H_2O and whose ir spectrum showed a band in the hydroxyl region. Hydrogen chloride and hydrogen bromide reacted easily with VI to form deliquescent adducts, both of which reacted with water to form stable salts with the composition VI + H_2O + HX (X = Cl or Br). The mass spectra of all these molecules showed strong peaks corresponding to VI, and also peaks for HX and (in the case of the hydrates) H_2O. These results suggest that the compounds have the following structures and are formed as indicated.



XVa, X = Cl
b, X = Br

XVIa, X = Cl
b, X = Br

10,9-Borazaronaphthalene (I)

The structure of I was formally indicated by elemental analysis, by its method of synthesis, and by its mass spectrum which showed a parent peak at *m/e* 129. The most convincing evidence came, however, from its extraordinary resemblance to the isoelectronic naphthalene, noted below.

(a) Both I and naphthalene form low-melting, colorless, volatile, flaky crystals, the odors of which are almost indistinguishable, and which both dissolve easily in nonpolar solvents.

(b) The X-ray powder photographs of I and naphthalene are superimposable, implying that they are isomorphous.

(c) The phase diagram (Figure 2) of the binary system I-naphthalene indicates that solid solutions form over the whole range of composition.

(d) The parent peak in the mass spectrum of I is also the base peak; this behavior is characteristic of aromatic systems (*e.g.*, naphthalene).

(e) The aromatic nature of I is further indicated by its resistance to aerial oxidation or hydrolysis, even in the presence of acid or alkali; this is in marked con-

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[9] N. S. Bhacca, D. P. Hollis, L. F. Johnson, and E. A. Pier, Varian Nmr Spectra Catalog, Varian Associates, Palo Alto, Calif., 1963.

[10] R. S. Rasmussen and R. R. Brattain, *J. Chem. Phys.*, **15**, 131 (1947).

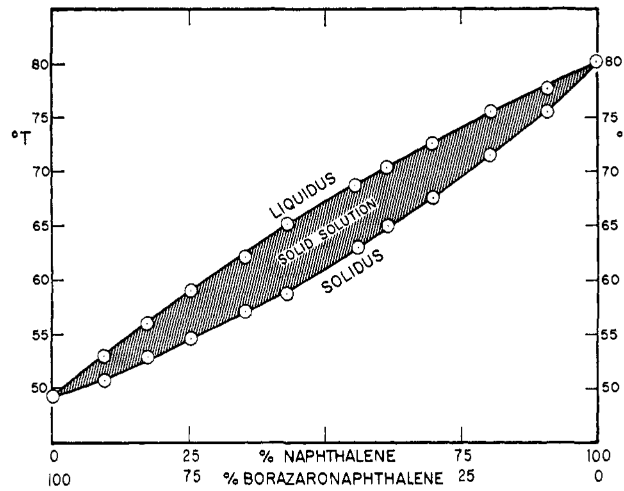

Figure 2. Phase diagram for the binary system naphthalene–10,9-borazaronaphthalene.

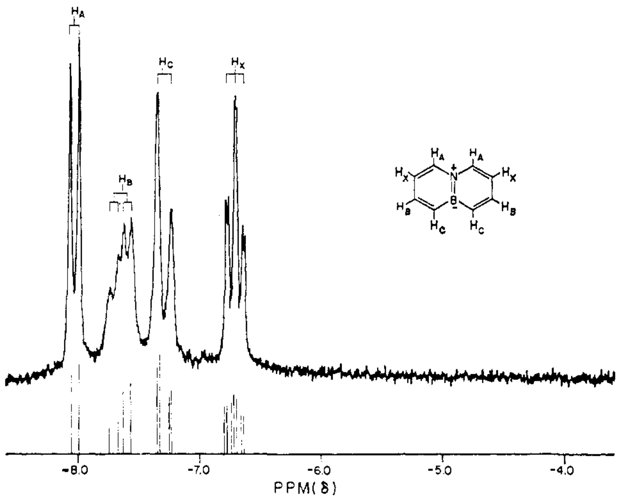

Figure 3. Proton nmr spectrum of I at 100 MHz and stick diagram of the simulated spectrum.

trast to the behavior of the analogous nonaromatic octahydro derivative VI.

(f) I forms a π-molecular complex with tetracyanoethylene which shows absorption (λ_{max} 518 nm) in the same region as the corresponding complex from naphthalene (λ_{max} 432 and 560 nm).

(g) I, like naphthalene, forms a stable crystalline picrate.

(h) The uv spectrum of I shows peaks at 236 nm (log ϵ 4.509), 2.42 nm (log ϵ 4.657), and 248 nm (log ϵ 4.487), in the expected[11] relationship to the first three π–π^* transitions of naphthalene.

These results suggest that I and naphthalene not only have similar geometries, but must also have very similar π systems, for otherwise there would be greater differences between their uv spectra, and between the charge-transfer spectra of complexes formed by them with tetracyanoethylene. This at first sight seems surprising, for, if the π-electron distributions were the same in both molecules, one would expect 10,9-borazaronaphthalene to be highly polar, having the dipolar

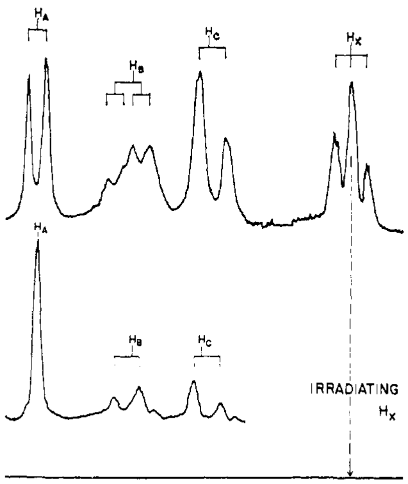

Figure 4. Effect of decoupling on the proton nmr spectrum of I.

structure indicated in I; yet its physical properties (low melting point and solubility in nonpolar solvents) indicate that its dipole moment must be small. The explanation probably lies in the facts that the BN σ bond in I must also be highly polar, with its moment in a direction opposite to that due to the π electrons, and that the polarity of this σ bond will increase with increasing negative charges on boron or positive charges on nitrogen. The reciprocal polarization of σ and π electrons may thus enable 10,9-borazaronaphthalene to be at once nonpolar, and to have a π-electron distribution corresponding reasonably closely to the dipolar resonance structure I.

Proton Nmr Spectrum of 10,9-Borazaronaphthalene

In the earlier investigation,[6] the proton nmr spectrum of I was measured only at 60 MHz, where the signals for the various protons are not sufficiently resolved for a first-order analysis to be unambiguous. The assignment given there was consequently somewhat uncertain. The spectrum has now been measured at 100 MHz by Dr. N. F. Chamberlain[12] who has also carried out decoupling experiments. These, together with theoretical considerations based on SCF MO calculations, permit an unambiguous assignment to be made.

The 100-MHz spectrum of I is shown in Figure 3. Since I has a plane of symmetry passing through boron and nitrogen and perpendicular to the rings, its nmr spectrum can be treated as that of a four-proton system. Figure 3 shows that the signals for all four protons are clearly resolved, Since coupling constants for protons *ortho* to one another in an aromatic ring are much larger than those for protons that are nonadjacent, the two doublet signals must correspond to the 1 and 4 protons, and the two multiplets to protons in the 2 and 3 positions.

When the signal due to the high-field multiplet is decoupled, the low-field multiplet collapses to a doublet (Figure 4), and the low-field doublet collapses to a singlet. The proton (X) corresponding to the high-field multiplet must therefore be adjacent to the proton (A) corresponding to the low-field doublet, and also adjacent to the proton (B) responsible for the low-field multiplet.

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[11] M. J. S. Dewar, V. P. Kubba, and R. Pettit, *J. Chem. Soc.*, 3073 (1958); M. J. S. Dewar and H. C. Longuet-Higgins, *Proc. Phys. Soc.*, 67, 795 (1954).

[12] Esso Research and Engineering, Baytown, Texas.

The low-field multiplet can therefore be interpreted as a quartet, due to coupling of proton B with proton X (J = 6 Hz) and proton C (J = Hz). The fact that the high-field multiplet appears as a triplet then indicates that the AX and BX couplings must be similar (~6 Hz). The fine structure in this triplet implies a long-range coupling to one of the other protons; this must be proton C, by elimination, an assignment confirmed by the fact that the low-field doublet (proton A) shows no trace of fine structure whereas that for proton C is slightly broadened. The fact that the signal for proton C shows no clear fine structure, corresponding to coupling with proton X, can probably be attributed to line broadening, due to quadrupole relaxation of an adjacent boron or nitrogen atom, for, as we have seen, the doublet signals in Figure 1 must correspond to the 1 and 4 protons, which are adjacent to nitrogen and boron, respectively.

This analysis shows that only two assignments of the protons A, B, C, X to the four positions 1(8), 2(7), 3(6), and 4(5) are possible; either A = 1, X = 2, B = 3, and C = 4, or C = 1, B = 2, X = 3, and A = 4. Now as was pointed out in the previous communication,[6] all theoretical treatments agree in predicting a much larger π-electron density at position 2 of I than at position 3. Since σ-inductive effects should be unimportant at the 2 and 3 positions of I, and since protons in both positions should be subject to similar magnetic effects due to aromatic ring currents, we can be almost certain that if there is any large difference between the chemical shifts for the two protons, then the upfield signal must correspond to proton 2. The observed spectrum (Figure 3) is therefore consistent only with the first assignment (A = 1, etc.).

Various attempts were made to confirm this assignment experimentally. One possibility lay in decoupling experiments, for, if the signal for the proton *ortho* to nitrogen were broadened by quadrupole relaxation of the nitrogen, decoupling nitrogen should lead to a narrowing of the proton signal. This experiment was carried out several times by Dr. W. B. Smith and Mr. J. Roark.[13] On one occasion the signal for proton A narrowed, but this result was not reproducible; on the other hand, the second doublet (proton C) showed no effect in any experiment. This result, which was unfortunately inconclusive, is at least consistent with our assignment; evidently the coupling of nitrogen to the adjacent proton is small, so decoupling of nitrogen has little effect on the proton signal.

Accurate values for the chemical shifts and coupling constants were determined by computer simulation of the spectrum; the results as shown in Table I. The coupling constants are in the usual range for *ortho* and *meta* couplings in aromatic rings, except for J_{34} which is unusually large (11.2 Hz). The final simulated spectrum is shown as a stick diagram at the foot of Figure 3.

These results can be used to get a rough estimate of the π-electron distribution in I. Assuming that the σ-inductive effects of boron and nitrogen are the same in I as in VI, and that the difference in chemical shift between α and β protons (due to ring current) is the same in I as in naphthalene,[14] we can estimate what the relative chemical shifts of the protons in I would be if the π electrons were uniformly distributed (as they are in naphthalene). Table II compares the values so estimated with those observed for I; the differences should be an indication of the deviations of the carbon atoms from neutrality. As pointed out in the previous communication,[6] this charge distribution is entirely different from what one would expect on the basis of resonance theory or simple HMO theory, both these theories predicting that atoms 1 and 3 should carry positive formal charges, and atoms 2 and 4 negative ones, the charges on atoms 1 and 4 being numerically the greater. The observed distribution agrees qualitatively with the results of preliminary SCF MO calculations,[6] a conclusion which has been fully confirmed by more detailed studies which will be reported elsewhere in due course.

Table I. Chemical Shifts and Coupling Constants Used to Simulate the Nmr Spectra of I at 100 MHz

Proton	Chemical shift, Hz[a]	Protons	Coupling constant, Hz
1 (≡A)	803.0	1,2	6.6
2 (≡X)	671.5	2,3	6.0
3 (≡B)	766.0	3,4	11.2
4 (≡C)	731.0	2,4	1.5
		1,3 and 1,4	0.0

[a] Relative to tetramethylsilane, measured at 100 MHz.

Table II. Deviations in the Chemical Shifts of Protons in I from Values Estimated for Uniform π-Electron Distributions

Position	Est chem shift,[a] δ	Obsd	Diff
1	9.11	8.03	−1.08
2	7.56	6.72	−0.84
3	7.56	7.66	+0.10
4	7.01	7.31	−0.30

[a] For uniform π-electron distribution.

Electrophilic Substitution in 10,9-Borazaronaphthalene

The deuteration of I was next studied. Preliminary MO calculations suggested that I should deuterate very readily, either in the 2,7 positions, or in the 4,5 positions, or both. Deuteration did in fact take place very readily when I was dissolved in dioxane containing deuteriosulfuric acid; the corresponding nmr spectrum, measured at 60 MHz in dioxane-d_8, is shown in Figure 5, while Figure 6 shows for comparison the corresponding spectrum of I in dioxane-d_8, containing normal sulfuric acid.

The spectrum of the deuterated material consists of two doublets and a multiplet. Substitution must therefore have taken place either at the 1,8 positions, or the 4,5 positions, since otherwise one pair of protons would have been left without *ortho* neighbors and should have given rise to a singlet. Comparison with Figures 2 and 6 shows that the protons displaced must in fact have been those in the 4 and 5 positions, adjacent to boron; this is in agreement with conclusions based on resonance theory, simple MO theory, and more sophisticated SCF

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(13) Department of Chemistry, Texas Christian University, Fort Worth, Texas.

(14) Values for naphthalene were taken from N. Jonathan, S. Gorgon, and B. P. Dailey, *J. Chem. Phys.*, 36, 2463 (1962).

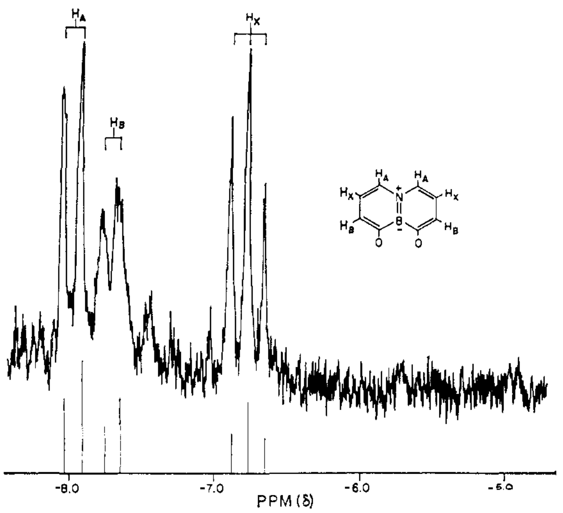


Figure 5. Proton nmr spectrum (60 MHz) of I in dioxane-d_8 containing 15% (v/v) sulfuric acid-d_2 and stick diagram of simulated specimen.

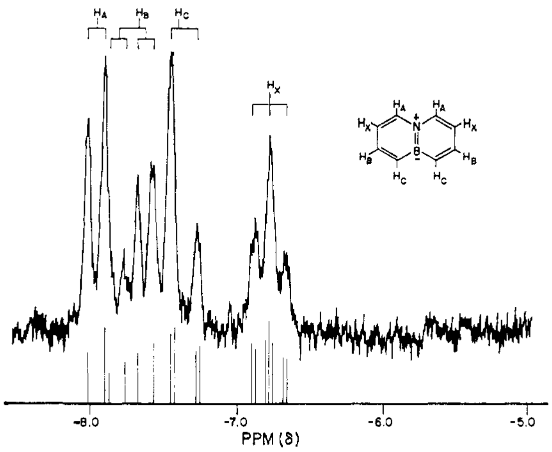
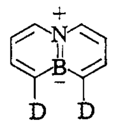
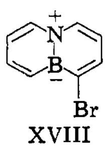


Figure 6. Proton nmr spectrum (60 MHz) of I in dioxane-d_8 containing 15% (v/v) normal sulfuric acid and stick diagram of simulated spectrum.

MO treatments. The product must therefore have been 4,5-dideuterio-10,9-borazaronaphthalene (XVII). An amusing confirmation of this is provided by the high-field signal in its nmr spectrum (Figure 5); this appears as a sharp triplet, unlike the corresponding signals in the spectrum of I (Figures 2 and 6), implying that the protons replaced by deuterium in XVI must be those responsible for the fine structure in the high-field multiplet of I. This fine structure must therefore be due to coupling between the 2 and 4 (or 5 and 7) protons, in agreement with the assignment deduced above.


XVII


XVIII

Final confirmation of the assignments of the spectra in Figures 5 and 6 was obtained by computer simulation; the simulated spectra are indicated by stick diagrams of the foot of each figure. The parameters deduced in this way are listed in Table II; it will be seen that they correspond closely to those in Table I if allowance is made for the differences in frequency. Similar results were also obtained from a comparison of the nmr spectra of I in deuteriotrifluoroacetic acid and in trifluoroacetic acid; the parameters used to simulate the observed spectra are also shown in Table III.

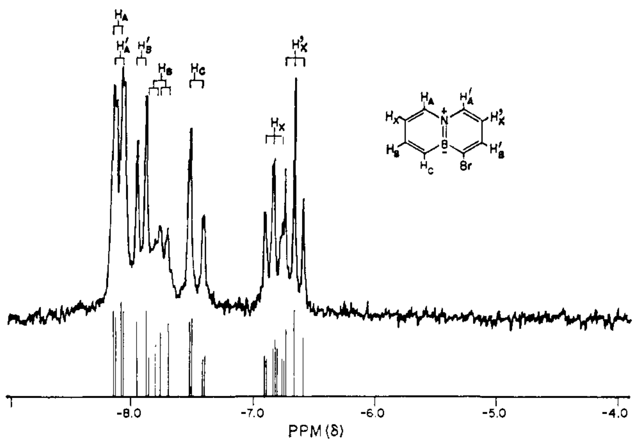


Figure 7. Proton nmr spectrum (100 MHz) of XVII in acetone-d_6.

Table III. Chemical Shifts and Coupling Constants Used to Simulate the Nmr Spectra of I and Its Dideuterio Derivative at 60 MHz

Solvent	δ_1[a]	δ_2[a]	δ_3[a]	δ_4[a]	J_{12}[b]	J_{23}[b]	J_{34}[b]	J_{24}[b]
Dioxane-d_8, D_2SO_4	477	405	461		7	7		
Dioxane-d_8, H_2SO_4	478	407	462	444	7	6	10	1
F_3CCOOD	469	404	465		7	7		
F_3CCOOH	469	404	466	449	7	7	10.5	1

[a] Chemical shifts in Hz relative to tetramethylsilane at 60 MHz.
[b] Coupling constant in Hz.

These results show that the 4 and 5 positions in I are very much more reactive than the others, for, while complete replacement of the 4 and 5 protons by deuterium took place rapidly in the cold in dioxane containing 15% of deuteriosulfuric acid, no further deuteration occurred even on prolonged standing. The nature of the product was also indicated by its mass spectrum which showed an intense peak at m/e 127, corresponding to I-d_2, and by its ir spectrum which showed bands at 2170, 2160, and 2135 K (C–D stretching).

Bromination of I with 1 mol of bromine in acetic acid gave a monobromo derivative, the proton nmr spectrum of which is shown in Figure 7.

The spectrum is naturally more complex than that of I or XVII, since the monobromo derivative lacks symmetry; however, it can be analyzed without difficulty by reference to Figure 3. Thus the spectrum contains two doublets, a triplet, and a quartet in essentially the same positions as those in Figure 3, being shifted about 0.2 ppm downfield. These must correspond to the four protons (A, B, C, X) in the unsubstituted ring. The peaks for the low-field doublet (A), and for the high-field triplet (X), are seen to be duplicated in Figure 7; this implies that the bromine atom does not occupy one of the corresponding positions. Furthermore, since the high-field signal remains a triplet, the bromine atom cannot occupy a position *ortho* to proton X (*i.e.*, positions 1 or 3). Substitution must therefore have taken place at position 4 (*i.e.*, replacement of proton C). If so, the proton in position B (3) of the bromine-containing ring should appear as a doublet; indeed, the only other additional peaks in Figure 7, over and above those in Figure 3, constitute a doublet, shifted downfield from the C quartet. The monobromo derivative must therefore have the structure XVIII, as would of course be expected from analogy with XVII. Further confirmation of this assignment comes from the structure of the high-field multiplet in XVIII. This consisted of two triplets, one sharp, the other split into three doublets ($J \sim 1$ Hz). The latter must correspond to proton C (5) in the unsubstituted ring, this being weakly coupled to proton X (2), as in I itself; the lack of fine structure in the second triplet is then accounted for if proton C (4) has been replaced by bromine. This incidentally provides an unambiguous distinction concerning the assignment of the two high-field triplets.

Experimental Section

Melting points are corrected. Unless otherwise stated, nmr spectra were recorded for 10% solutions in carbon tetrachloride or chloroform-*d* with a Varian A-60 spectrometer. The ir spectra of solids were measured in KBr disks, and of liquids as thin films, using a Beckman IR8 spectrometer. The uv-visible spectra were measured with a Beckman DK 2A spectrometer, the solvent being 95% ethanol unless otherwise stated. Small-scale glpc separations were carried out on columns of silicone gum rubber or Carbowax ($^1/_8$ in. i.d.) using an Aerograph Model 1520 chromatograph; large-scale separations were carried out using similar columns ($^3/_8$ in. i.d.) with an Aerograph A700 Autoprep chromatograph.

4-Hydroxy-1-butene (III). This was prepared by a modification of the method of Roberts and Mazur.[15] A stirred mixture of 1,3-butanediol (2 l.) and *p*-toluenesulfonic acid (200 g) was heated until distillation commenced; additional diol was added slowly to keep the volume of the reaction mixture constant. Distillation was continued until the boiling point reached 130° (*ca.* 60 hr, 7.5 l. of diol reacted). The distillate was extracted with ether, washed with sodium bicarbonate solution, dried ($MgSO_4$), and distilled through a 1-m column packed with glass helices to give crude 4-hydroxy-1-butene (1870 g), bp 111–114° (lit.[15] 115° (770 mm)), n^{27}D 1.4145 (lit.[15] n^{25}D 1.4182).

Di-3-butenylamine (V). 4-Hydroxy-1-butene was converted to 4-bromo-1-butene (IVb) by the method of Linstead and Rydon.[16] The bromide (50 g) and liquid ammonia (60 ml) were heated in a stainless steel autoclave to 100° for 10 hr. Water was added to the residue in the autoclave and the amine isolated with ether and distilled. The fraction bp 70–78° (70 mm) was redistilled through a Teflon spinning-band column with a reflux ratio of 100:1, giving V (8.7 g), 95% pure by glpc, bp 75–76° (48 mm). An analytical sample, prepared by glpc, had n^{26}D 1.4396.

Anal. Calcd for $C_8H_{15}N$: C, 76.74; H, 12.07; mol wt, 125. Found: C, 76.42; H, 12.00; mol wt (mass spectroscopy), 125.

3-Butenylbutylamine (VIII). Preparative glpc of the crude amine (bp 70–78° (70 mm)) described above gave a fraction identified as VIII, n^{26}D 1.4232, with a shorter retention time than V.

Anal. Calcd for $C_8H_{17}N$: C, 75.52; H, 13.47; mol wt, 127. Found: C, 75.39; H, 13.32; mol wt (mass spectroscopy), 127.

3-Butenyl-*trans*-2-butenylamine (VII). A second glpc fraction from crude V, with a longer retention time than V, proved to be VII, n^{26}D 1.4456.

Anal. Calcd for $C_8H_{15}N$: C, 76.74; H, 12.07; mol wt, 125. Found: C, 76.38; H, 11.76; mol wt (mass spectroscopy), 125.

9-Aza-10-boradecalin (VI). Diborane, prepared by slow addition of a solution of sodium borohydride (4.75 g) in dry diglyme (100 ml) to one of boron trifluoride etherate (26.6 g) in dry diglyme (10 ml) under argon at −10°, was passed into a stirred solution of di-3-butenylamine (12.5 g) in dry toluene (800 ml), also at −10°. When addition was complete, the solution was left at room temperature overnight and then boiled under reflux for 24 hr. Distillation of the product under argon gave 9-aza-10-boradecalin (8.79 g) as a colorless oil, bp 81–84° (27 mm); an analytical sample, purified by glpc, had n^{24}D 1.4837.

Anal. Calcd for $C_8H_{16}BN$: C, 70.12; H, 11.77; B, 7.71; N, 10.22; mol wt, 137. Found: C, 70.07; H, 11.75; B, 7.71; N, 10.30; mol wt (mass spectroscopy), 137.

10-Hydroxydecahydro-10,9-borazaronaphthalene (XIV). A solution of VI (500 mg) in aqueous acetone (20 ml of 10%) was boiled under reflux for 30 min and the solution then evaporated to dryness, giving XIV (480 mg) as colorless prisms, mp 115–120°, raised by recrystallization from nitromethane to 119–121°.

Anal. Calcd for $C_{16}H_{18}BNO$: C, 61.77; H, 11.70; B, 6.97; N, 9.03. Found: C, 61.76, H, 11.60; B, 6.82; N, 9.00.

9-Aza-10-boradecaline Hydrochloride (XVa). Dry hydrogen chloride was passed into a solution of VI (1.0 g) in dry ether (25 ml) giving XVa (1.0 g) as a colorless deliquescent solid.

Anal. Calcd for $C_8H_{17}BClN$: C, 55.38; H, 9.87; B, 6.23; Cl, 20.43; N, 8.07. Found: C, 55.48; H, 9.89; B, 6.15; Cl, 20.62; N, 8.08.

6-Hydroxy-1-aza-6-boracyclodecane Hydrochloride (XVIa). Exposure of XV to air gave XVIa which crystallized from nitromethane in colorless rhombs, mp 187.5–189.5°.

Anal. Calcd for $C_8H_{19}BClNO$: C, 50.17; H, 10.00; B, 5.65; N, 7.31. Found: C, 49.99; H, 9.40; B, 6.19; N, 7.02.

6-Hydroxy-1-aza-6-boracyclodecane Hydrobromide (XVIb). Treatment of XVI with dry hydrogen bromide gave XVIb as an extremely deliquescent yellow solid which on exposure to air formed colorless crystals of XVIb, mp 165–167° after recrystallization from nitromethane.

Anal. Calcd for $C_8H_{19}BBrNO$: C, 40.72; H, 8.11; N, 5.93. Found: C, 41.34; H, 7.94; N, 6.19.

10,9-Borazaronaphthalene (I). A solution of VI (5 g) in 1-octene (50 ml) was heated with palladized charcoal (5 g of 10%) in a stainless steel autoclave for 24 hr at 300°. A small portion of the resulting solution was submitted to glpc; if no I was present, more catalyst (5 g) was added and the heating repeated. The product was chromatographed from hexene on basic alumina, giving I (35% yield) which sublimed in large colorless flakes, mp 48–49°, with an odor almost identical with that of naphthalene.

Anal. Calcd for C_8H_8BN: C, 74.50; H, 6.25; B, 8.38; N, 10.86; mol wt, 129. Found: C, 74.29; H, 6.40; B, 8.51; N, 10.65; mol wt (mass spectroscopy), 129.

The picrate crystallized from ethanol as a yellow powder, mp 133.5–134.5°.

Anal. Calcd for $C_{14}H_{11}BN_4O_7$: C, 47.28; H, 3.18. Found: C, 46.96; H, 3.09.

Bis(2-methoxy-3-butenyl)amine (XII). A mixture of 4-iodo-3-methoxy-1-butene[8] (60.9 g) and liquid ammonia (100 ml) was heated 22 hr at 100° in a stainless steel autoclave. The product was poured into water and the amine isolated with ether and distilled, giving XII (35% yield) as a colorless liquid, bp 46–48.5° (2 mm), n^{25}D 1.4441.

Anal. Calcd for $C_{10}H_{19}NO_2$: C, 64.82; H, 10.34; N, 7.56. Found: C, 64.83; H, 10.40; N, 7.54.

The hydrochloride, prepared in ether, crystallized from ethyl acetate in white needles, mp 107.5–108.5°.

Anal. Calcd for $C_{10}H_{20}ClNO_2$: C, 54.17; H, 9.09; Cl, 15.99; N, 6.32. Found: C, 54.46; H, 9.04; Cl, 16.15; N, 6.12.

The N-benzoyl derivative (XIIb), prepared by the Schotten–Baumann method, distilled at 148–152° (1.3 mm) as a colorless oil, n^{25}D 1.5146.

Anal. Calcd for $C_{17}H_{23}NO_3$: C, 70.56; H, 8.07; N, 4.84. Found: C, 70.68; H, 8.09; N, 4.92.

4-Amino-3-methoxy-1-butene (XIII). This amine, isolated as a byproduct from the preparation of XIIa, bp 30–35° (3.5 mm), was converted to its hydrochloride, mp 136–137° after recrystallization from ethyl acetate.

Anal. Calcd for $C_5H_{12}ClNO$: C, 43.64; H, 8.79; Cl, 25.76; N, 10.18. Found: C, 43.57; H, 8.85; Cl, 25.72; N, 10.13.

4-Bromo-10,9-borazaronaphthalene (XVIII). Bromine (39 μl) was added to a solution of I (100 mg) in glacial acetic acid (2 ml) when an immediate reaction took place with formation of hydrogen

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(15) J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, 73, 2509 (1951).

(16) R. P. Linstead and H. N. Rydon, *J. Chem. Soc.*, 1998 (1934).

bromide. The solution was poured on ice and extracted with ether; the ether layer was washed, dried, and evaporated, leaving XVIII which after recrystallization (twice) from hexane formed colorless plates (50 mg), mp 62.5–64°.

Anal. Calcd for C_8H_7BBrN: C, 46.23; H, 3.39; Br, 38.44. Found: C, 46.15; H, 3.48; Br, 38.22.

Acknowledgment. We are very grateful to Dr. N. F. Chamberlain[12] for the nmr measurements on I and XVIII, and to Dr. W. B. Smith and Mr. J. Roark[13] for the attempt to identify the protons in I by nitrogen decoupling.

The Structure of the Benzilic Acid Rearrangement Product of 3*α*,17*β*-Diacetoxy-11-hydroxy-12-oxo-5*β*-androst-9(11)-ene. An Unusual Structure with Three Five-Membered Rings *cis*-Fused

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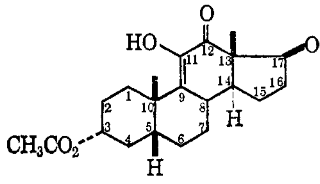
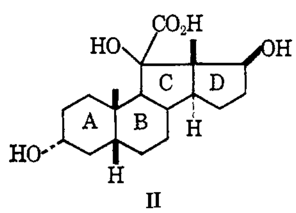
Contribution from the W. A. Noyes Chemical Laboratory, University of Illinois' Urbana, Illinois 61801. *Received October 11, 1967*

Abstract: The benzilic acid rearrangement product of 3*α*,17*β*-diacetoxy-11-hydroxy-12-oxo-5*β*-androst-9(11)-ene has been shown to be 3*α*,11*α*,17*β*-trihydroxy-11*β*-carboxy-13*α*-C-nor-5*β*-androstane-11*β*-carboxylic acid 11a,17-lactone by the results of a single-crystal X-ray analysis on a *p*-bromobenzoyl ester of the product. The heavy atom derivative crystallizes in the space group $P2_12_12_1$, with $a = 16.76 \pm 0.03$, $b = 7.05 \pm 0.01$, and $c = 19.58 \pm 0.03$ Å, and with four molecules of $C_{26}H_{31}O_5Br$ in the unit cell. The detailed conformation of the steroid derivative is discussed and compared with other related compounds. The effect of severe steric compression in the *cis*-fused five-membered rings on the rest of the molecule is noteworthy.

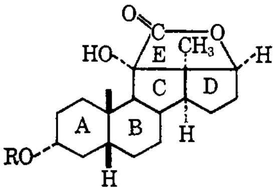
The steroid derivative 3*α*,17*β*-diacetoxy-11-hydroxy-12-oxo-5*β*-androst-9(11)-ene (I), when treated with base, gives a compound $C_{19}H_{28}O_4$, which can be shown to contain two hydroxyl groups and a lactone ring.[1] A benzilic acid rearrangement of I would be expected to give initially II. Lactonization of II between the carboxyl group on C(11) and the hydroxyl group at C(17) would be impossible on steric grounds with a *trans* C/D ring junction.[1] To account for the experimental facts, a retroaldol equilibrium, with epimerization at C(13 leading to a *cis* C/D ring junction prior to the benzilic acid rearrangement, was postulated and the structure IIIa was proposed for the lactone.[1] During the course of this transformation numerous keto–enol equilibria could lead to a change of stereochemistry of the B/C as well as the C/D ring junctions.



I



II



IIIa, R = H
b, R = *p*-BrC_6H_4CO

A crystal structure analysis was carried out on a *p*-bromobenzoyl ester of the rearrangement product to confirm the structural proposals and to establish the geometry of the unusual *cis*-fused five-membered ring system. A preliminary report of this work has been published.[2]

Experimental Section

A crystalline sample of the *p*-bromobenzoyl ester of the rearrangement product was kindly supplied by Dr. Paul Kurath of Abbott Laboratories, Chicago, Ill. The crystals are colorless needles, mp 250–251°.

Crystal data for $C_{26}H_{31}O_5Br$ were $M = 503.4$; orthorhombic; $a = 16.76 \pm 0.03$, $b = 7.05 \pm 0.01$, $c = 19.58 \pm 0.03$ Å; $V = 2313.5 \times 10^{-24}$ cm^3; $\rho_{\text{meas}} = 1.42$ g cm^{-3}; $Z = 4$; $\rho_{\text{calcd}} = 1.45$ g cm^{-3}; $F(000) = 1048$; systematic absences: $h00$ when $h = 2n + 1$; $0k0$, when $k = 2n + 1$; $00l$, when $l = 2n + 1$; space group $P2_12_12_1(D_2^4)$; linear absorption coefficient $\mu(\text{Cu K}\alpha) = 29.6$ cm^{-1}. The cell dimensions were determined from precession photographs using Mo Kα radiation ($\lambda = 0.7107$ Å). The density was determined by flotation in an aqueous zinc chloride solution.

Equiinclination Weissenberg photographs (Cu Kα radiation) were taken on a fine needle mounted about the *b* crystallographic axis. The levels $h0l$ to $h6l$ were recorded at 25°, with the X-ray generator settings at 35 kV and 20 ma. Visual estimates gave a total of 1493 independent nonzero intensity measurements. Corrections were made for Lorentz and polarization effects, but not for absorption.

Structure Determination

The coordinates of the bromine atom were readily determined from the three Harker sections of the three-

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(1) P. Kurath, *Experientia*, **22**, 657 (1966); *J. Org. Chem.*, **32**, 3626 (1967).

(2) J. S. McKechnie and I. C. Paul, *Experientia*, **23**, 612 (1967).