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TETRAZADIBORINANES; ACETYLATION AND REACTION WITH ISOCYANATES

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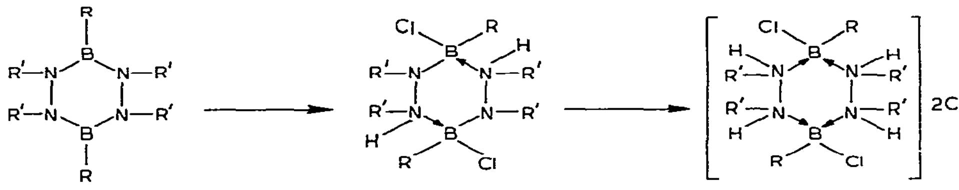
SUMMARY

Reaction of 3,6-diphenyl-1,2,4,5-tetraza-3,6-diborinane with methyl isocyanate has been shown to give a bis addition product, probably at the 1 and 4 positions. Both monomeric tetrazadiborinanes and dimeric cage tetrazadiborinanes react with acetic anhydride in the presence of acid with ring opening to provide acetylated diboryl hydrazines. Acetic anhydride reacts with monomeric diphenyltetrazadiborinane in the presence of an acid scavenger to give a bis acetylated compound similar to the isocyanate addition product. An unusual chemical shift in the NMR spectrum of this compound is probably caused by diamagnetic shielding of the acetyl methyl by the phenyl group on boron.

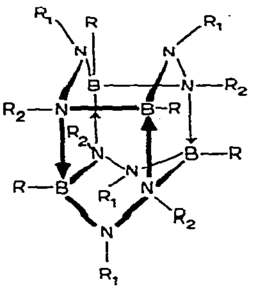
INTRODUCTION

Monomeric tetrazadiborinanes were first described in 1960[1]. The chemistry of this system has not been thoroughly studied but hydrolysis[2] and alcoholysis[3] have been shown to provide the parent boronic acids or esters and the expected hydrazine. Controlled addition of hydrogen chloride provides 2/1 adducts (II) and 4/1 adducts (III)[2]; at higher temperatures, the B–N bonds are cleaved. Addition products of monomeric tetrazadiborinanes with one equivalent of the Lewis acids BF_3, BCl_3 and $FeCl_3$ have been described[3,4] but the structures of the products have not been rigorously defined. Secondary amines have been shown to react with tetrazadiborinanes with ring opening followed by reclosure to a new five-membered ring[2].



(I) (II) (III)

Recently, cage dimers (IV) of tetrazadiborinanes have been described[5-7].



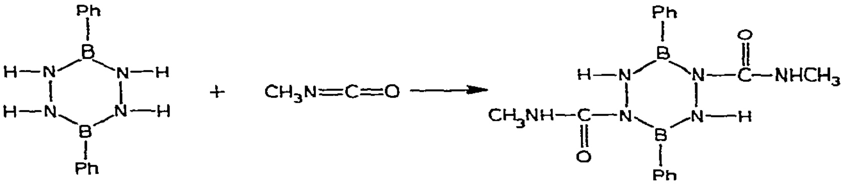
(IV)

Reactions of these dimers with methyl isocyanate have been shown to occur at the trigonal nitrogens in stepwise manner although monosubstitution was not observed[6]. Two equivalents of hydrogen chloride add to (IV) ($R=H$, $R_1=R_2=CH_3$) while addition of Lewis acids is complicated[4]. Boron trichloride has been shown to add one equivalent to (IV) ($R=R_1=H$, $R_2=CH_3$)[4].

The reaction of monomeric tetrazadiborinanes with isocyanates in comparison with the well-defined reaction of dimer, and comparative reactions of the monomers and dimers with acetic anhydride are the subject of this paper.

RESULTS AND DISCUSSION

The reaction of methyl isocyanate with the tetrazadiborinane dimer (IV) ($R=$t-Bu, $R_1=R_2=H$) has been shown to occur in stepwise fashion with attack occurring at the trigonal positions[6]. Complete reaction provides a product in which each six-membered tetrazadiborinane ring of the dimer has been substituted in the 1 and 4 positions; the 2 and 5 positions are, of course, not nucleophilic because of their coordinate covalent bond with the boron in the second ring. Reaction of monomeric 3,6-diphenyl-1,2,4,5-tetrazadiborinane (I, $R=Ph$, $R'=H$) with excess methyl isocyanate in methylene chloride solution led to the uptake of two equivalents of the isocyanate and provided a high melting (>300°) white solid product. Structure (V) has been assigned to this material on the basis of infrared and nuclear magnetic resonance spectra and elemental analysis. The coupling of the $-NH-CH_3$ system which is observed in the NMR is indicative of simple addition of the isocyanate and excludes possible insertion into the B–N bond[8,9] which would lead to the structure $>B{-}N(CH_3){-}C(O){-}N<$ and a singlet for the methyl group in the NMR. Simple addition at the positions indicated is to be expected in analogy with the product

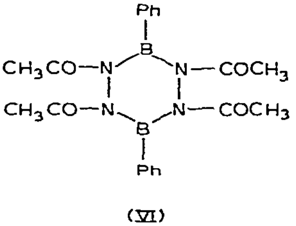


(V)

[IV, R = t-Bu, $R_1 = -C(O)-NHCH_3$, $R_2 = H$] obtained from the reaction of four equivalents of methyl isocyanate with the cage dimer. Although the position of attack on the six-membered ring has not been definitely established, the other possibility, in which attack occurs at the 1,5-positions, does not appear as likely as (V).

Acetylation reactions on nitrogens bearing a boron are not well known. We have examined acetylation of the cage dimer (IV, R = t-Bu, $R_1 = R_2 = H$) and of the monomeric diphenyl tetrazadiborinane (I, R = Ph, R′ = H). Treatment of the cage compound with acetyl chloride led to a variety of products from which no pure materials were successfully isolated. Acetylation of the tert-butyl cage dimer with acetic anhydride in the presence of a trace of concentrated sulfuric acid, however, led to the formation of a new product, m.p. 141–142°, in good yield. The infrared spectrum indicated that complete acylation had occurred by the absence of any NH absorption; two carbonyl peaks appeared at 1625 and 1720 cm^{-1}. The nuclear magnetic resonance spectrum showed only three absorptions; these were originally attributed to a singlet for the methyls of the tert-butyl groups, and two singlets for the methyls of two different kinds of acetyl groups. These data were suggestive of complete acylation of the cage structure [IV, R = t-Bu, $R_1 = R_2 = -C(O)-CH_3$]. In such a structure, the two acetyl groups should indeed be different; those on the trigonal nitrogens should occur at lower wavelength in the IR and at higher field in the NMR. The apparent ease of attack at the nontrigonal nitrogens in the acetylation compared with the lack of reactivity of isocyanates at these positions was disturbing however. Elemental analytical data could not be rationalized with the completely acylated cage structure; the nitrogen content was considerably low whereas boron was about what was expected. Plausible structures for the acylated cage product were not apparent at this point. The product appeared relatively stable to hydrolysis since it was isolated from an aqueous workup, but slow decomposition to boric acid suggested possible air oxidation.

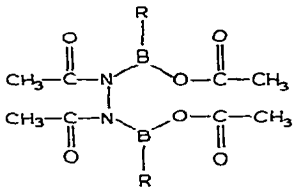
Acetylation of 3,6-diphenyl-1,2,4,5-tetraza-3,6-diborinane (I) was then examined and an unusual product obtained. Two types of carbonyl groups (IR 1630 and 1715 cm^{-1}) which are quite similar to those observed in the infrared of the acetylated cage product were again apparent. The proton NMR spectrum was also similar to that of the acetylated cage product in that only two absorptions other than those due to phenyl hydrogens were observed. Again no N–H absorptions were present in either IR or NMR spectra. These data cannot support formulation as the completely acylated structure (VI) unless one invokes some conformational structures to explain differences in carbonyl groups. The elemental analysis confirmed that the product did not possess structure VI.



(VI)

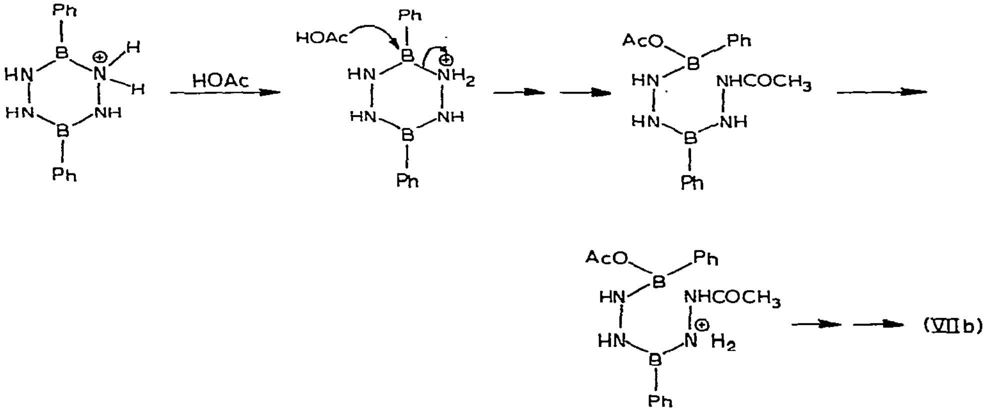
Mass spectral data were quite helpful in assigning structures to these acetylated materials. The mass spectrum of the acylated 3,6-diphenyl-1,2,4,5-tetraza-3,6-diborinane product had the peak of highest mass at *m/e* 408. If this is taken as the molecular ion M, the cleavage pattern at lower masses exemplifies the presence of phenyl and acetyl groups. The presence of two borons can be observed as part of the resulting fragments with masses of 169 or greater. All of the fragments, as is true for the parent, are four atomic mass units greater than expected on the basis of structure (VI). The mass spectrum of the acetylated cage compound apparently did not contain a molecular ion peak, but an ion at *m/e* 353 might possibly represent M minus a methyl group. If this were the case, M would be 368; this is four atomic mass units greater than 1/2 the completely acetylated cage compound. Ions observed in the spectrum follow a pattern of 368 minus (x tert-butyls$+y$ acetyls)$\pm n$H ($n=1$ or 0). Ions corresponding to tert-butyl are observed at 57 and 55 and acetyl at 43.

The above data suggest that the acylated compounds are of similar structure and that two oxygen atoms are present in the compounds in place of two nitrogen atoms; the elemental analyses support this suggestion and the IR and NMR can be easily explained if one assumes the presence of esters [$-O-C(O)-CH_3$] as well as amides [$-N(R)-C(O)-CH_3$]. Structure (VII) was proposed to fit the data. Thus ring cleavage and degradation of the cage compound and of the six-membered tetrazadiborine ring to a common structure have been observed.



(VII) a, R=t-Bu
b, R=Ph

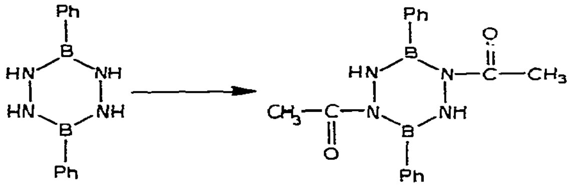
The following rationale for the reaction is suggested. The acetic anhydride contained some sulfuric acid and water and thus, some acetic acid. The first step of the reaction is probably protonation of a nitrogen followed by displacement with acetic



acid. The liberated amine is probably then acylated. The adjacent nitrogen must then be protonated to arrive at the observed product. Facile ring opening of (I) with acetic acid has been demonstrated; phenylboronic anhydride is obtained by dissolution of (I) (R = Ph) in glacial acetic acid.

A thermal decomposition product from diphenyltetrazadiborinane, a high melting solid whose structure has not been determined, has been described[6]. It is not a cage dimer and is not the simple six-membered ring, but it too gives compound (VIIb) when treated with acetic anhydride in the presence of sulfuric acid, thus demonstrating that the B–N–N–B structure is present.

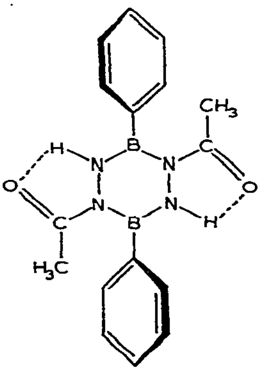
If no proton source is available during acetylation, ring opening is not observed in the case of monomeric 3,6-diphenyl-1,2,4,5-tetrazadiborinane. Acetic anhydride containing suspended sodium carbonate to scavenge any acid provides good yields of the diacylated compound (VIII), which was originally expected on the basis of the isocyanate reaction. The cage tert-butyl compound (IV) gave a mixture of products, including (VIIa) when treated in similar fashion. No acylated cage product could be isolated pure.



(I) (VIII)

Attempted acylation of (VIII) with acetic anhydride containing a small amount of sulfuric acid demonstrated that this compound is not an intermediate in the formation of (VIIb). No reaction was detected and (VIII) was reisolated.

The NMR spectrum of (VIII) is interesting. It is as expected except that the acetyl methyl resonance is much too far upfield (1.33 ppm) for a normal acetamide type methyl (about 2 ppm)[10]. Prior studies have demonstrated that the ring is planar[2]. Models indicate that if hydrogen bonding between the hydrogen on the ring nitrogen and the carbonyl oxygen occurs, the methyl group of the amide would be situated directly over the phenyl ring whose plane should lie perpendicular to the plane of the tetrazadiborinane system. This, of course, would lead to strong diamagnetic shielding and an upfield shift[11,12].



A recent publication[13] suggests that the material employed in this study as monomeric diphenyltetrazadiborinane actually contains higher polymer. A compound of m.p. 64–65° is briefly described as the pure monomer. One attempt to prepare this low melting material gave a white solid of broad melting range starting at 57°. Acetylation of the impure sample gave VIIb in somewhat lower yield than from the material previously described[3,14] as the monomeric tetrazadiborinane.

EXPERIMENTAL

3,6-*Diphenyl*-1,2,4,5-*tetraza*-3,6-*diborinane* (*I*)

The method of Niedenzu, Beyer, and Dawson[14] was employed. A solution of 18.7 g (0.0106 mole) of bis(dimethylamino)phenylborane in 30 cc of dry n-hexane was added slowly to a stirred mixture of 3.5 g (0.011 mole) of hydrazine in 25 cc of n-hexane cooled in a dry-ice bath. No apparent reaction occurred. The mixture was allowed to warm to room temperature and after a few minutes a white solid began to precipitate. The mixture was stirred vigorously for 1½ h and then filtered. The white solid product was dried overnight in vacuum at room temperature to give 11.5 g (92% yield) of (I). The material partially melted at about 150° and then resolidified and melted at 258–260°. Titration with perchloric acid in acetic acid gives an equivalent weight of 120.

Reaction of methyl isocyanate with 3,6-*diphenyl*-1,2,4,5-*tetraza*-3,6-*diborinane* (*I*)

To a cloudy solution of 2.36 g (0.01 mole) of 3,6-diphenyl-1,2,4,5-tetraza-3,6-diborinane in 100 cc of methylene chloride was added 3.0 g (0.052 mole) of methyl isocyanate. The mixture was allowed to stand at ambient temperature for 2 h and was then filtered. The volatile materials were removed by distillation and the residue was dissolved in 100 cc of methylene chloride and filtered through filter-aid. The solution was extracted with 50 cc of 10% aqueous hydrochloric acid and washed with two 50 cc portions of water. The methylene chloride layer was dried over magnesium sulfate and stripped to give 3.2 g (91% yield) of a white solid. Recrystallization from methanol/acetone provided white crystals, m.p. >300°. (Found: C, 55.10; H, 6.04; B, 6.25; N, 24.05. $C_{16}H_{20}B_2N_6O_2$ calcd.: C, 54.91; H, 5.76; B, 6.18; N, 24.01%.)

The infrared spectrum contained N–H absorptions 3430, 3230 and 3195 cm^{-1} and a carbonyl band at 1650 cm^{-1}. The proton NMR spectrum showed the CH_3–NH–C(O)– system at 2.32 ppm (d) and 3.84 ppm (q). The phenyl absorptions 7.70 and 7.32 ppm have a sharp singlet in their midst at 7.54 ppm for the NH; this band disappears on addition of D_2O.

Reaction of acetic anhydride with (*I*)

To a solution of 10 cc of acetic anhydride containing one drop of concentrated sulfuric acid was added 0.5 g (2.13 mmole) of 3,6-diphenyl-1,2,4,5-tetrazadiborinane (I) in small portions over a 5 min period. The solid partially dissolved and then the mixture was heated on the steam bath for 10 min during which time the solid completely dissolved and the solution turned yellow. Cooling the mixture resulted in 0.41 g of solid crystallizing. After collecting this on a filter, the filtrate was poured into water and the mixture was stirred. As the anhydride hydrolyzed, a solid was deposited. This material, 0.25 g, was collected on a filter and shown to be identical with the first fraction. Total yield 0.66 g (75%); m.p. 205–207°. (Found: C, 58.94; H, 5.51; B, 5.38;

N, 6.50. $C_{20}H_{22}B_2N_2O_6$ calcd.: C, 58.87; H, 5.43; B, 5.30; N, 6.86%.)

The infrared spectrum of a nujol mull contained no N–H absorptions, but two carbonyls were apparent at 1630 and 1715 cm^{-1}. The proton NMR spectrum has two singlets at 2.03 and 2.15 ppm assignable to methyl groups of the amide and ester respectively and phenyl absorptions at 7.60 and 7.22 ppm. Integration shows a ratio of 3/3/5 of methyl/methyl/phenyl. Molecular weight calculated 408, mass spectrum 408.

Reaction of acetic anhydride with 3,6-*di-tert-butyl*-1,2,4,5-*tetraza*-3,6-*diborinane dimer* (*IV*)

A 0.5 g (1.27 mmole) sample of (IV) was dissolved in 10 cc of acetic anhydride and two drops of concentrated sulfuric acid were added. The mixture was heated on a steam bath for 15 min and then poured into 150 cc of water. The mixture was stirred for 1 h and the insoluble material, 0.56 g (59% yield), was collected on a filter and dried. Recrystallization from ether-low boiling petroleum ether gave white crystals which appeared to contain some boric acid. Sublimation in vacuum gave a white solid, m.p. 141–142°, which produced boric acid on standing in the air. (Found: C, 52.12; H, 8.21; B, 6.31; N, 8.03. $C_{16}H_{30}B_2N_2O_6$ calcd.: C, 52.21; H, 8.22; B, 5.88; N, 7.61%.)

The IR shows no N–H absorption and contains carbonyl group absorptions at 1625 and 1720 cm^{-1}. One absorption appears in the NMR at 0.85 ppm for the methyls on tert-butyl groups. Two other absorptions are present in the spectrum due to the methyls on the acetyl groups; these appear as single bands at 2.02 and 2.30 ppm. The mass spectrum showed peaks with a pattern of 368–(x tert-butyls + y acetyls) $\pm nH$. Calculated mol.wt. 368.

Reaction of (*I*) *with acetic anhydride and sodium carbonate*

To a suspension of 1.0 g of sodium carbonate in 20 cc of acetic anhydride was added slowly and in small portions 1.0 g (4.25 mmole) of 3,6-diphenyl-1,2,4,5-tetraza-3,6-diborinane (I) over a 1 h period. The mixture was allowed to stand at room temperature for 2 h and was then poured into water. An oily insoluble layer of the anhydride and product slowly deposited a solid as the anhydride hydrolyzed. A white solid, 1.24 g (89% yield), was collected on a filter and was recrystallized from methylene chloride/acetone, m.p. >300°. (Found: C, 59.81; H, 5.56; B, 6.77; N, 17.54. $C_{16}H_{18}B_2N_4O_2$ calcd.: C, 60.06; H, 5.67; B, 6.76; N, 17.51%.)

The infrared spectrum contained one carbonyl adsorption at 1640 cm^{-1} and an N–H band is apparent at 3170 cm^{-1}. The proton NMR has a sharp singlet at 1.33 ppm for the methyls of the acetyl groups; this is at unusually high field probably due to shielding by the phenyl rings. The phenyl absorptions appear at 7.59 and 7.96 ppm and the ring N–H at 8.84 ppm in the expected ratios.

Attempted reaction of 3,6-*diphenyl*-1,4-*diacetyl*-1,2,4,5-*tetraza*-3,6-*diborinane* (*VIIb*) *with acetic anhydride*

To 10 cc of acetic anhydride containing one drop of concentrated sulfuric acid was added 0.5 g of (VIIb). The solid dissolved as the mixture was heated on the steam bath for 10 min. The solution was poured into water and 0.46 g of solid precipitated. The infrared spectrum indicated that no reaction had occurred.

Reaction of 3,6-*diphenyl*-1,2,4,5-*tetraza*-3,6-*diborinane* (*I*) *with acetic acid*

One gram of (I) was added to 10 cc of glacial acetic acid and the mixture was heated on the steam bath for 30 min. The mixture was allowed to cool and the solid which precipitated, 0.28 g, m.p. 215–217°, was collected on a filter. Comparison of the infrared spectrum with that of an authentic sample demonstrated that the product was phenylboronic anhydride.

REFERENCES

1 H. NÖTH, *Angew. Chem.*, 72 (1960) 40.
2 H. NÖTH AND W. REGNET, *Z. Naturforsch. A*, 18 (1963) 1138.
3 H. NÖTH AND W. REGNET, *Boron–Nitrogen Chemistry, Advances in Chemistry Series*, No. 42, American Chemical Society, Washington, 1964, p. 166.
4 H. NÖTH AND W. REGNET, *Chem. Ber.*, 102 (1969) 2241.
5 J. J. MILLER AND F. A. JOHNSON, *J. Amer. Chem. Soc.*, 90 (1968) 218.
6 J. J. MILLER AND F. A. JOHNSON, *Inorg. Chem.*, 9 (1970) 69.
7 H. NÖTH AND W. REGNET, *Chem. Ber.*, 102 (1969) 167.
8 H. BEYER, J. W. DAWSON, H. JENNE AND K. NIEDENZU, *J. Chem. Soc.*, (1964) 2115.
9 R. H. CRAGG, M. F. LAPPERT AND B. P. TILLEY, *J. Chem. Soc.*, (1964) 2108.
10 L. M. JACKMAN, *Applications of N.M.R. in Organic Chemistry*, Pergamon Press, New York, 1959, p. 57.
11 J. S. WAUGH AND R. W. FESSENDEN, *J. Amer. Chem. Soc.*, 79 (1957) 846.
12 D. J. PASTO AND C. R. JOHNSON, *Organic Structure Determination*, Prentice-Hall, Englewood Cliffs, 1969, p. 72.
13 C. UNGURENASU, S. CIHODARU AND I. POPESCU, *Tetrahedron Lett.*, (1969) 1435.
14 K. NIEDENZU, H. BEYER AND J. W. DAWSON, *Inorg. Chem.*, 1 (1962) 738.