

**395.** *Boron–Nitrogen Compounds. Part XI.*<sup>1</sup> *The Reaction of Some Boron–Nitrogen Compounds with Organic Isocyanates.*

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Aminoboranes added across the N=C linkage of organic isocyanates and isothiocyanates to yield *N*-boronated urea derivatives; hydrolysis studies substantiate suggested structures.

THE easy preparation of isocyanate and isothiocyanate derivatives of boron compounds from the corresponding boron halides and a salt of cyanic or thiocyanic acid has recently been reported.<sup>2</sup> The reaction of organic isocyanates and isothiocyanates with boron compounds has not been so well explored; a patent claims the formation of thermally stable polymers from an organoboric acid and bifunctional isocyanates through the elimination of carbon dioxide,<sup>3</sup> but these results could not be confirmed.<sup>4</sup> Boric acid condenses with phenyl isocyanate in the presence of triethylamine to form trisphenylaminoborane.<sup>5</sup> The copolymerization of *B*-trisubstituted borazines with hexamethylene di-isocyanate to yield polymers (I), has been described;<sup>6</sup> this reaction would indicate a relatively high reactivity of the NH groups in borazines. However, when tri-*B*-methylborazine was treated with acetyl chloride no reaction was observed below 100°.<sup>7</sup> Boone

<sup>1</sup> Part X, *Chem. Ber.*, 1963, 2653.

<sup>2</sup> Goubeau and Grabner, *Chem. Ber.*, 1960, **93**, 1379; Brennan, Dahl, and Schaeffer, *J. Amer. Chem. Soc.*, 1960, **82**, 6248; Green, Sowerby, and Wihsne, *Chem. and Ind.*, 1960, 1306; Lappert and Pyszora, *Proc. Chem. Soc.*, 1960, 350.

<sup>3</sup> Upson, U.S. Patent 2,517,944/1940.

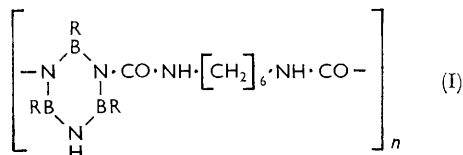
<sup>4</sup> Ruigh, WADC Technical Report 55-26, Parts I—IV, 1955—56.

<sup>5</sup> Aries, U.S. Patent 2,931,831/1960.

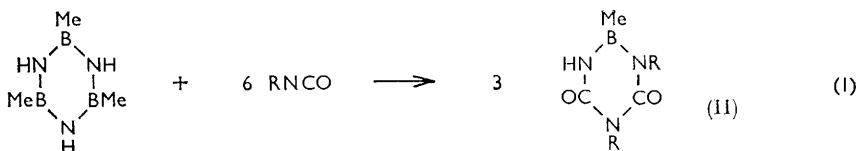
<sup>6</sup> Korshak, Bekasova, Azmyatina, and Aristorkhova (*Chem. Abs.*, 1961, **55**, 25,349).

<sup>7</sup> Abs. of Papers, 142nd National Meeting, Amer. Chem. Soc., Atlantic City, N.J., 1962, p. 6N.

and Willcockson<sup>7</sup> suggest that Korshak's interpretation of the experimental data is erroneous: isocyanates react with borazines through cleavage of the B-N ring with the formation of a new ring system (eqn. 1). Analogous observations have been made in



our laboratory and by Cragg and Lappert.<sup>8</sup> The experimental results are consistent but do not exclude the possibility of oxygen atoms in the ring and imido-groups on the carbon atoms, or of both *R* groups being on the nitrogen atoms adjacent to boron.

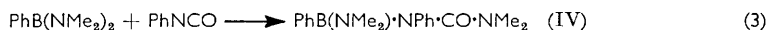


The present work is concerned with the reaction of isocyanates (and isothiocyanates) with aminoborane B-N linkages, where the formation of *N*-boronated ureas and thioureas is likely; two other groups have investigated similar problems.<sup>8,9</sup>

We found the reaction of monoaminoboranes with isocyanate proceeds smoothly (eqn. 2), and with bis(dimethylamino)phenylborane and phenyl isocyanate a step-wise



mechanism was observed (eqns. 3 and 4), in which the second step can be effected only under extreme forcing conditions and does not yield a pure and uniform product. Since migration of the *B*-phenyl groups was not observed, this suggests in conjunction with previous results,<sup>10</sup> a surprising series of reactivities of groups attached to boron with isocyanates:  $\text{NR}_2 > \text{Ph} > \text{Cl}$ .



When tris-*B*-(diethylamino)borazine was treated with isocyanates in inert solvents, neither reaction of the NH group<sup>6</sup> nor depolymerization of the borazine ring and subsequent rearrangement to the ring structure (II) (eqn. 1) was observed. Rather, migration of the exocyclic amino-group occurred, leading to *B*-ureido-groups (VI)<sup>11</sup> (eqn. 5). The



formation of such compounds (VI) seems to indicate a greater bond strength for the B-N ring linkage than for the exocyclic B-N bonds of tris-*B*-aminoborazines. Similar observations have been made in other reactions of these compounds.<sup>12</sup> The contrast between this reaction and that between tris-*B*-(diethylamino)tri-*N*-ethylborazine with phenyl isocyanate<sup>8</sup> illustrates that the nature of the borazine ring is widely influenced by *N*-substituents. Under similar mild conditions tri-*B*-chloroborazine does not react with

<sup>8</sup> Cragg and Lappert, personal communication; see also Preprints of Papers, Internat. Symp. on Boron-Nitrogen Chem., Durham, N.C., U.S.A., April 1963; Cragg, Lappert, and Tilley, preceding paper.

<sup>9</sup> Heying, personal communication; see also Preprints of Papers, Internat. Symp. on Boron-Nitrogen Chem., Durham, N.C., U.S.A., April 1963.

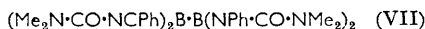
<sup>10</sup> Lappert and Prokai, *J.*, 1963, 4223.

<sup>11</sup> Lappert and Pyszora, *J.*, 1963, 1744.

<sup>12</sup> Niedenzu, Harrelson, and Dawson, *Chem. Ber.*, 1961, 94, 671.

phenyl isocyanate; with more stringent conditions gummy, viscous materials of unknown structure are formed. However, borazine itself reacted smoothly with isocyanates even at low temperatures.

Tris(dimethylamino)borane also reacted with phenyl isocyanate under mild conditions to yield tris-(*N'**N'*-dimethyl-*N*-phenylureido)borane only,<sup>9</sup> and tetrakis(dimethylamino)-diboron gave the tetrakisureido-derivative (VII).



All the products obtained on the addition of aminoboranes across the N=C linkage of phenyl isocyanate are relatively unstable. It has been difficult to obtain pure products and in most cases we were unable accurately to determine the molecular weight. Yields of the principle products also varied widely. However, structures (III)—(VII) are substantiated by elemental analysis, and hydrolysis provides the *N*-substituted urea which can be identified in all cases. Treatment of (IV) with *NN*-dimethylhydrazine yielded *NN*-dimethyl-*N'*-phenylurea and bis-(*N'**N'*-dimethylhydrazino)phenylborane.<sup>13</sup>

The infrared spectra of the *N*-boronated ureas and thioureas are complex and it is difficult to assign definite group frequencies. However, it is easily recognized that in compounds (IV) and (V) the original *B*-phenyl link has been preserved (strong, sharp absorption at 1440—1450 cm.<sup>-1</sup> with small shoulders at the high-frequency side denoting a <sup>10</sup>B isotope effect<sup>14</sup>). The typical NCO and NCS absorptions could not be detected in the infrared spectra of the products; instead, frequencies near 1243 cm.<sup>-1</sup> (CO group in ureas) and 1143 cm.<sup>-1</sup> (C=S in thioureas) were recorded.

In the infrared spectra of tris-*B*-ureidoborazines (VI) the NH stretch was recognized as a relatively weak absorption near 3460 cm.<sup>-1</sup>. A much stronger band, observed near 3300 cm.<sup>-1</sup>, might indicate a large percentage of associated NH groupings (a high degree of association seems reasonable for a molecule with such structure). The broad NCO absorption of isocyanates is lacking in the spectrum, but CO bands are recognized. In addition, hydrolysis and subsequent isolation of the expected *N*-substituted urea lends credence to the suggested structures.

#### EXPERIMENTAL

*Reaction of a Monoaminoborane with Phenyl Isocyanate* (eqn. 2).—(Diethylamino)dipentylborane<sup>1</sup> (5.6 g., 0.025 mole) in *n*-hexane (15 c.c.) was added to phenyl isocyanate (3.0 g., 0.025 mole) in *n*-hexane (25 c.c.), and the mixture was stirred at room temperature for 30 hr. Upon evaporation of the solvent and distillation in a vacuum B-(*N'**N'*-diethyl-*N*-phenylureido)dipentylborane (5.4 g., 63%), b. p. 133—134°/7 mm., was obtained (Found: B, 3.4; N, 8.0; C, 73.3; H, 11.0. C<sub>21</sub>H<sub>37</sub>BN<sub>2</sub>O requires B, 3.1; N, 8.1; C, 73.3; H, 10.9%).

*Reaction of Bis(dimethylamino)phenylborane with Phenyl Isocyanate* (eqn. 3).—Phenyl isocyanate (12.1 g., 0.11 mole) in hexane (25 c.c.) was added to bis(dimethylamino)phenylborane (17 g., 0.1 mole) in benzene (200 c.c.), and the mixture refluxed for 3 hr. Distillation in a vacuum afforded B-dimethylamino-(*N'**N'*-dimethyl-*N*-phenylureido)phenylborane, b. p. 60—64°/4 mm., melting range 82—95° (Found: B, 3.7; N, 13.9; C, 68.4; H, 7.3. C<sub>17</sub>H<sub>22</sub>BN<sub>3</sub>O requires B, 3.7; N, 14.2; C, 69.2; H, 7.5%).

Similarly, B-dimethylamino-(*N'**N'*-dimethyl-*N*-ethylureido)phenylborane, b. p. 72—78°/2 mm. (Found: B, 5.1; N, 18.1; C, 60.1; H, 9.9. BN<sub>3</sub>C<sub>13</sub>N<sub>22</sub>O requires B, 4.6; N, 17.9; C, 61.3; H, 9.4), was obtained from ethyl isocyanate and bis(dimethylamino)phenylborane, and B-dimethylamino-(*N'**N'*-dimethyl-*N*-phenylthioureido)phenylborane, b. p. 81—84°/3 mm. (Found: B, 3.4; N, 13.4; C, 63.4; H, 7.5; S, 10.7. C<sub>17</sub>H<sub>22</sub>BN<sub>3</sub>S requires B, 3.5; N, 13.6; C, 65.5; H, 7.1; S, 10.3%) from bis(dimethylamino)phenylborane and phenyl isothiocyanate.

*Reaction according to Eqns. (3) and (4)*.—Refluxing bis(dimethylamino)phenylborane with a large excess of phenyl isocyanate for 12 hr. yielded a yellow, unsublimable solid. Boron and nitrogen analyses indicated the formation of (IV) (Found: B, 2.9; N, 13.8. Calc. for

<sup>13</sup> Niedenzu, Beyer, and Dawson, *Inorg. Chem.*, 1962, **1**, 738.

<sup>14</sup> Wyman, Niedenzu, and Dawson, *J.*, 1962, 4068.

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$C_{24}H_{27}BN_4O_2$ : B, 2·6; N, 13·5). However, the material melted over a wide range and subsequent attempts at purification failed.

*Reaction of (IV) with NN-Dimethylhydrazine.*—Upon refluxing (IV) with *NN*-dimethylhydrazine (2 mols) in benzene, *NN*-dimethyl-*N'*-phenylurea and bis-(*N'*-dimethylhydrazino)-phenylborane<sup>17</sup> were the only products.

*Reaction of Tris-B-(diethylamino)borazine with Phenyl Isocyanate.*—A phenyl isocyanate (22 g., 0·2 mole) in hexane (25 c.c.) and tris-*B*-(diethylamino)borazine (14·7 g., 0·05 mole) in hexane (200 c.c.) were mixed and refluxed for several hours, solvent and excess of phenyl isocyanate removed, and the residue distilled in a vacuum to yield *tris-B-(N'N'-diethyl-N-phenylureido)borazine*, b. p. 163—165°/4 mm. (Found: B, 5·3; N, 19·0; C, 60·5; H, 9·0.  $C_{33}H_{48}B_3N_9O_3$  requires B, 5·0; N, 19·4; C, 60·8; H, 7·4%). Analogously *tris-B-(N'N'-diethyl-N-phenylthioureido)borazine*, m. p. (recrystallized from hexane) 128°, was obtained (Found: B, 4·6; N, 16·0; C, 54·2; H, 7·2; S, 12·0.  $C_{33}H_{48}B_3N_9S_3$  requires B, 4·6; N, 18·05; C, 56·5; H, 6·9; S, 13·7%).

*Reaction of Tetrakis(dimethylamino)diboron with Phenyl Isocyanate.*—To phenyl isocyanate (25 g., 0·21 mole) in hexane (60 c.c.; dried over sodium), tetrakis(dimethylamino)diboron (10 g., 0·05 mole) in hexane (20 c.c.) was added. The white precipitate of (VII), had m. p. 142—158° (from hexane) (Found: B, 3·4; N, 16·2.  $C_{36}H_{44}B_2N_4O_4$  requires B, 3·2; N, 16·6%).

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