# Boron–Sulphur Compounds. Part IV.[1] Synthesis, Reactions, and Mass Spectral Studies of some Substituted 4-Methyl-1,3,2-dithiaborolans

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The preparation and properties of derivatives of 4-methyl-1,3,2-dithiaborolan are described and the mass spectral fragmentations of $\underline{S\cdot CH_2\cdot CH](Me)\cdot S\cdot B}Ph$ and $\underline{S\cdot CH_2\cdot CH(Me)\cdot S\cdot B}NEt_2$ are fully discussed.

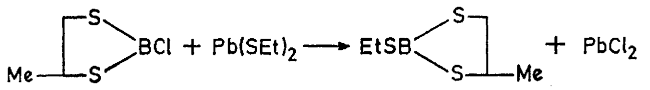
THERE has been considerable interest over the last decade in the synthesis and properties of heterocyclic organoboranes. Much of this interest has been concerned with boron–oxygen[2] and boron–nitrogen[3] heterocyclic systems and, by comparison, organoboron heterocyclic compounds containing boron–sulphur bonds with three exceptions[2,4,5] have been completely ignored. There has recently been an increasing interest in the chemistry of thioboranes due to their use as synthetic intermediates in the preparation of organosulphur compounds.[6-9] We therefore report the results of our study on derivatives of 4-methyl-1,3,2-dithiaborolans. The physical properties of the compounds prepared are given in the Table.

The well established reaction of boron trichloride or phenylboron dichloride in a 1 : 1 molar ratio with a dithiol, was found to be very successful in the preparation of the 2-chloro- and 2-phenyl-4-methyl-1,3,2-dithiaborolans. These two compounds were thermally stable but hydrolytically very unstable.

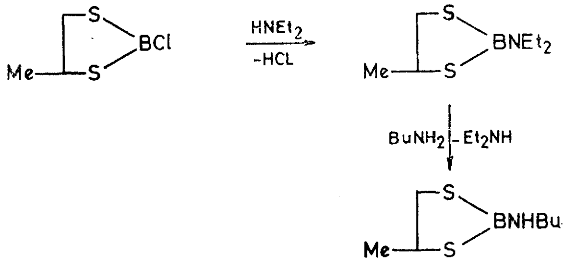
$$RBX_2 + HS\cdot CH(Me)\cdot CH_2\cdot SH \longrightarrow \underline{S\cdot CH(Me)\cdot CH_2\cdot S\cdot B}R$$

$$R = Ph \text{ or } Cl$$

The first preparation of an alkylthio-derivative of a dithiaborolan was achieved by the action[10] of lead ethanethiolate on a chloroborolan. This method works very well for the synthesis of thioboranes. Attempts to prepare compounds of this type by the reaction of 2-chloro-1,3,2-dithiaborinan and butanethiol failed,[4] although it is possible that if lead butanethiolate been used instead of butanethiol then the reaction might have been successful.

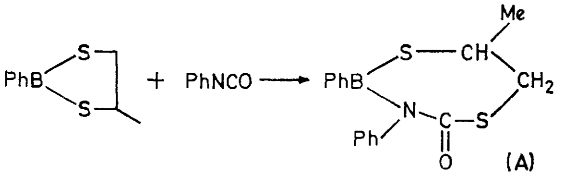


Diethylamine reacted readily with the chloroborolan to give the corresponding dialkylamino-derivative from which the butylamino-derivative was obtained by transamination. The two compounds are the first examples of two new classes of compounds, with the exceptions of the corresponding dialkylamino-derivative of a borthiin[11,12] in which a boron atom is bonded to one nitrogen and two sulphur atoms. The 2-ethylthio-4-methyl-1,3,2-dithiaborolan has unusual stability in that the boron–sulphur bond is not cleaved by hydrogen chloride.



*Reactions with Phenyl Isocyanate.*—Aminoboranes[13] and thioboranes[10,14] have been reported to react readily with phenyl isocyanate. We found that phenyl-, diethylamino-, and ethylthio-4-methyl-1,3,2-dithiaborolans all reacted readily with phenyl isocyanate to give the corresponding ureido- and thioureido-boranes. Where possible the insertion reaction took place exocyclically in preference to reaction in the ring.

The reaction of phenyl isocyanate with the phenyl compound is of interest because it caused ring expansion.



(A)

Compound (A) was characterised by analysis, the presence of a carbonyl band at 1660 cm$^{-1}$ and mass spectral analysis showed the molecular weight to be 313. Al-

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[1] Part III, R. H. Cragg, J. F. J. Todd, and A. F. Weston, *J.C.S. Dalton*, 1972, 1373.

[2] S. G. Shore, J. L. Crist, B. Lockman, J. R. Long, and A. D. Coon, *J.C.S. Dalton*, 1972, 1123.

[3] K. Niedenzu and C. D. Miller, *Fortsch. chem. Forsch.*, 1970, 191.

[4] A. Finch and J. Pearn, *Tetrahedron*, 1964, **20**, 173.

[5] A. Finch, P. J. Gardner, and E. J. Pearn, *Trans. Faraday Soc.*, 1966, **62**, 1072.

[6] B. M. Mikhaikov and N. S. Fedotov, *Izvest. Akad. Nauk, S.S.S.R., Otdel Khim. Nauk*, 1962, 999.

[7] A. Pelter, T. Levitt, and K. Smith, *Chem. Comm.*, 1969, 435.

[8] R. H. Cragg and J. P. N. Husband, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 773.

[9] R. H. Cragg and J. P. N. Husband, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 221.

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

[11] E. Wiberg and W. Sturm, *Angew. Chem.*, 1955, **67**, 483.

[12] J. A. Forstner and E. L. Muetterties, *Inorg. Chem.*, 1966, **5**, 164.

[13] R. H. Cragg, M. F. Lappert, and B. P. Tilley, *J. Chem. Soc.*, 1964, 2108.

[14] R. H. Cragg, *J. Chem. Soc.* (*A*), 1968, 2962.

though ring expansions of this type have been reported for aminoboranes[12] this is the first example for a thioborane.

Phenyl isocyanate reacted readily with the diethylamino-compound to give the corresponding ureidoborane; this readily hydrolysed. The mass spectrum of the ureidoborane gave the parent peak at 308. A peak at 192, due to PhNHCONEt$_2$ was also observed, resulting from the hydrolysis of the parent compound. This indicated that the isocyanate had reacted across the exocyclic B–N bond in preference to the cyclic B–S bonds. The ethylthio-compound reacted readily with phenyl isocyanate to give the corresponding thioureidoborane; this readily hydrolysed. The mass spectrum showed the parent peak at 297. A peak at 181, assigned to PhNHCOSEt, was observed, resulting from hydrolysis of the parent compound. This indicates that the isocyanate reaction had (*a*) reacted across the exocyclic B–S bond in preference to the cyclic B–S bonds, and (*b*) that the product of the addition was a 1 : 1 reaction.

Properties of some 4-methyl-1,3,2-dithiaborolans

| Compound | B.p. | $^{11}$B n.m.r.[a] | Molecular weight[b] Theory | Found | $n_D^{25}$ |
|---|---|---|---|---|---|
| S·CH(Me)·CH$_2$·S·BCl | 58/6 mm | −41·8 | | *c* | 1·5490 |
| S·CH(Me)·CH$_2$·S·BPh | 83/0·1 mm | −53·3 | 194 | 194 | 1·6125 |
| S·CH(Me)·CH$_2$·S·B·SEt | 86/3 mm | −51·1 | 178 | 178 | 1·5754 |
| S·CH(Me)·CH$_2$·S·B·NEt$_2$ | 87/3·5 mm | −31·1 | 189 | 189 | 1·5228 |
| S·CH(Me)·CH$_2$·S·B·NHBu | 86/1·5 mm | *c* | 189 | 189 | 1·5229<br>(27°) |

[a] (MeO)$_3$B external std. [b] By mass spectrometry. [c] Not measured.

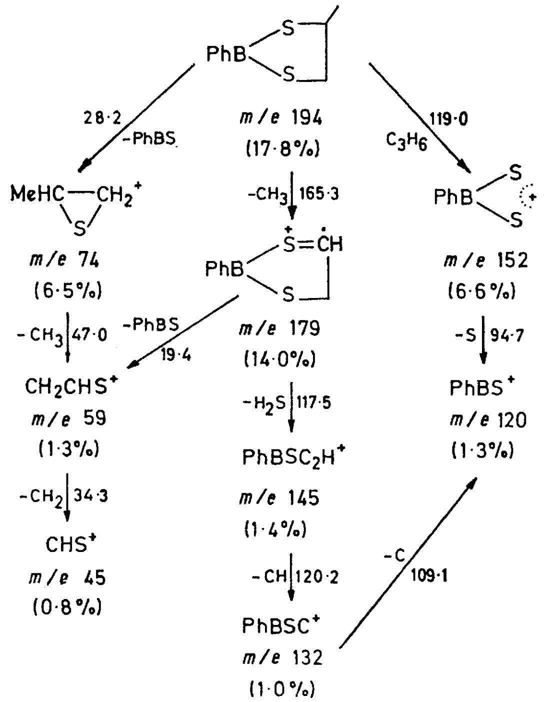
### *Mass Spectra*

With the exception of 2-phenyl-1,3,2-dithiaborolan[15] there have been no detailed studies of the mass spectra of heterocyclic organoboranes containing two sulphur atoms. We therefore report our findings on (*a*) 4-methyl-2-phenyl-1,3,2-dithiaborolan and (*b*) 2-diethylamino-4-methyl-1,3,2-dithiaborolan. The former compound is discussed to see what effect, if any, the introduction of the methyl substituent had on the fragmentation of the compound compared to the unsubstituted compound. The latter compound is discussed since with the introduction of a nitrogen atom a further site to take the positive charge is involved and we wanted to investigate what effect this had on the fragmentation of the ring. The mass spectra results (see Table) show that these compounds are monomeric in the gaseous phase.

(a) 4-*Methyl*-2-*phenyl*-1,3,2-*dithiaborolan*.—The fragmentation pattern based on observed metastable ions coupled with metastable scanning is given in Scheme 1. The mass spectrum of this compound was always accompanied by trace amounts of the dithiol, whose spectrum was removed by computer analysis. The parent compound (I) can fragment *via* the cleavage of one of three bonds.

Process 1 produces a reduced-ring species whilst processes 2 and 3 although isomerically different lead to the same empirical result, and hence they will be discussed simultaneously.

(1) *Rearrangement followed by phenyl ring expansion.* Although peaks 119/118 were observed, their intensities were 6·7 and 14·3 respectively and no metastable could be found in support of this fragmentation process. This can be explained by the fact that since the ion produced would not be a very stable species and its production by processes 2 and 3 would be hindered in either case by the methyl group the rearrangement would only be possible when the methyl conformation permitted.



SCHEME 1 Fragmentation pattern for 4-methyl-2-phenyl-1,3,2-dithiaborolan (the percentages are expressed in terms of total ionisation)

(2) *Rearrangement to produce sulphur–hydrocarbon*

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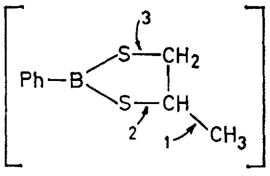
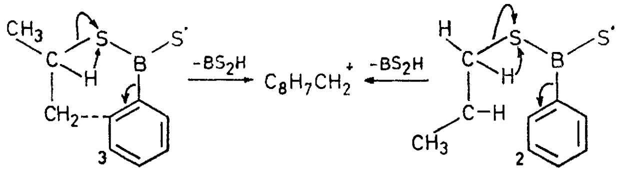
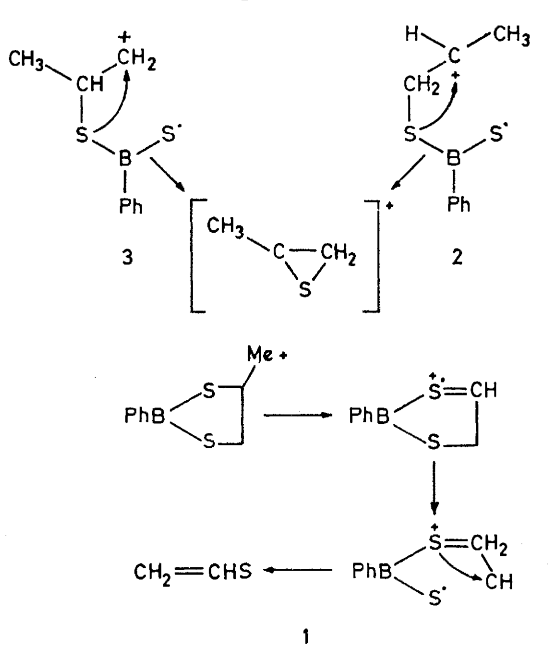
[15] R. H. Cragg, G. Lawson, and J. F. J. Todd, *J.C.S. Dalton*, 1972, 878.

*fragments*. The formation of sulphur–hydrocarbon fragments can be produced by processes 2 and 3 whilst the second step *via* process 1 will produce a smaller fragment of the same type. This can be demonstrated by the following scheme in which all the ions represented have been characterised by metastable analysis. Rearrangements can also occur *via* the loss of a hydrocarbon fragment from the ring. This fragmentation process is confirmed by the presence of an ion at *m*/*e* 42/41 corresponding to the rearranged unsaturated hydrocarbon (with possible loss of H) and also an ion *m*/*e* 27. Finally the loss of $H_2S$ from the ion of *m*/*e* 179 was verified, although only a minor fragment, by metastable analysis.


(I)

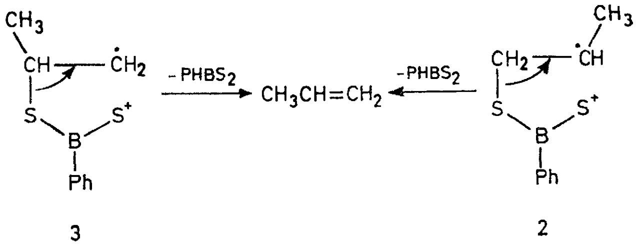


The following conclusions can be made. (1) The addition of a methyl group to the ring did not essentially alter the fragmentation of the borolan ring compared to that of the unsubstituted compound. It did however hinder to a large extent the production of the expanded phenyl ring by limiting conformations in which ring expansion could take place.

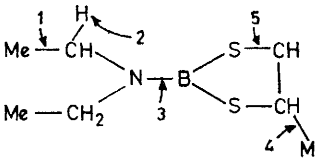


(2) The loss of methyl from the ring produced a very stable ion which fragmented only slightly to lower ions.

(3) The cleavage of C–S bonds resulting in either cyclic thia or $PhBS_2$ formation accounted for the major part of the remaining ion percentage after methyl loss was accounted for.

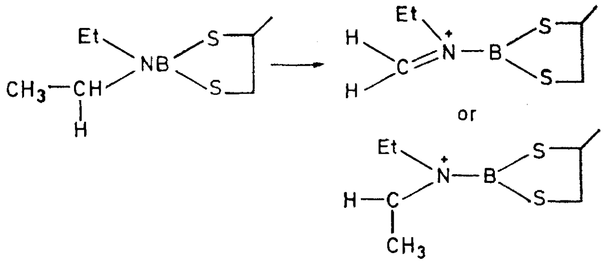


(b) 2-*Diethylamino-4-methyl*-1,3,2-*dithiaborolan*.— The fragmentation pattern based on observed metastable ions coupled with metastable scanning is given in Scheme 2. The introduction of a dialkylamino-group as the exocyclic group introduced a new centre for the positive charge, in the positive ions. There are now five possible positions where cleavage can take place:

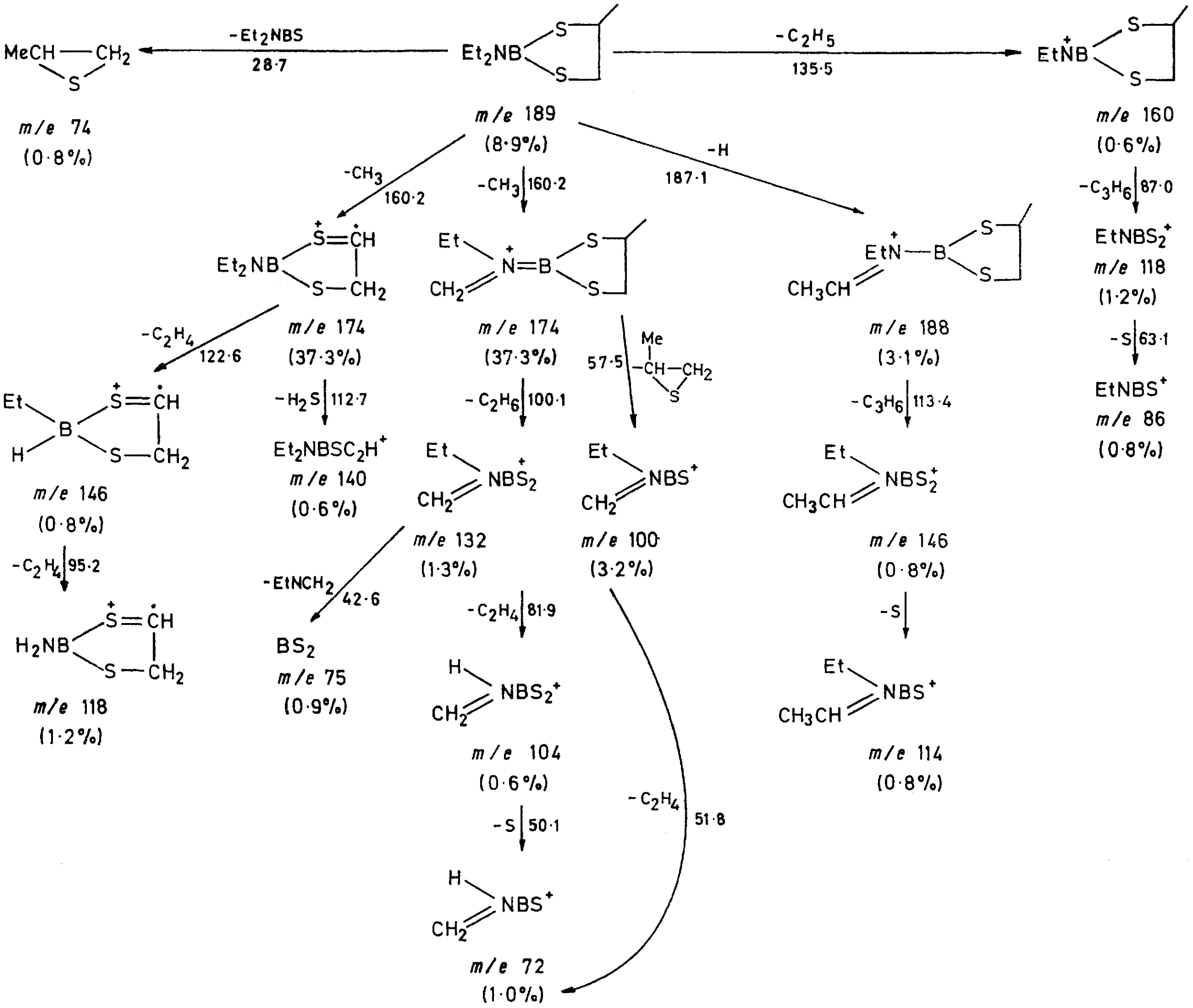


In the compound previously discussed demethylation of the ring *via* 4, gave a peak which was 79% of the base peak. Hence by analogy 21% of the ion of *m*/*e* 174 peak is due to the demethylated ring compound and the other 79% is due to the loss of methyl from the amine chain *via* 1. Hence demethylation of the ring prior to loss from the amine chain was a major fragmentation route and a metastable was seen for secondary loss though the fragment produced was >1% of base. Instead fragmentation proceeded by amine chain loss *via* an ion of *m*/*e* 146 and an ion of *m*/*e* 118. In contrast, other ring fragmentations, by comparison with the phenyl case, *via* 5 were very minor and the formation of ion of *m*/*e* 147 $Et_2NBS_2$ was not observed and neither were its subsequent fragments.

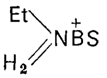
The major fragmentations were *via* route 1, *i.e.* loss of $CH_3$ from the amine hydrocarbon chain—an α fission where the positive change is centred on nitrogen.

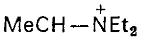


Thus, subsequent fragmentations would take place only where neutral ring fragments were lost without the necessity of charge balancing in the ring, *i.e.* methyl ring loss from an ion of *m/e* 174 was impossible as was loss of cyclic thiahydrocarbon. Alternatively neutral hydrocarbon could be lost to give an ion of *m/e* 132. This was followed by loss of $C_2H_4$ from the ethyl group remaining to give an ion of *m/e* 104. The loss of sulphur from an ion of *m/e* 132 was a minor process and $BS_2$ was a minor product. The analogous α fission, route 2, also took place with the loss of H from the parent but this was a comparatively minor route. The loss of an ethyl group was also a minor process and further fragmentations were *via* loss of neutral molecules from the ring. One ion which is of interest is *m/e* 100. Precise mass measurement showed the ion to be (a) and not (b) which could have been formed *via* the rearrangement of a MeCH group from the ring which has been observed in the mass spectra of phenyl-1,3,2-dioxaborolans. Hence the following conclusions can be made. The replacement of a phenyl group by the diethylamino-group introduced a new major centre for the positive charge which caused ring fragmentations to be less important. The nitrogen atom took over as the main charge centre and all fragmentations revolved round it. Once the $N^+$ was formed only neutral ring species could be lost and no charge could be formed in the ring. The loss of the ring methyl to give $S^+$ was the only occasion when S was charged and also in loss of amine side chain fragments from the stable demethylated ion.



SCHEME 2 Fragmentation pattern for 2-diethylamino-1,2,3-dithia-4-methyl-borolan (the percentages are expressed in terms of total ionisation)

(a) 

(b) 

$MeCH{-}\overset{+}{N}Et_2$

## EXPERIMENTAL

*General Procedures.*—Solvents were dried over sodium wire and distilled before use. The $^{11}B$ n.m.r. were recorded as neat liquids, with methyl borate as an external standard, and using a Perkin-Elmer R10 spectrometer. The mass spectra were recorded using an A.E.I. MS902 mass spectrometer at 70 eV. The source was maintained at 170 °C and the compounds were introduced as neat liquids or solids using an unheated direct-insertion probe. In general only those peaks of relative intensity greater than 5% were considered. The usual precautions were taken with air-sensitive starting materials and products.

*Reaction between Boron Trichloride and Propane*-1,2-*dithiol*. Propane-1,2-dithiol (20·25 g, 0·19 mol) was added slowly to boron trichloride (25 g, 0·21 mol) at −78°. The mixture was allowed to come to room temperature when the evolution of HCl became noticeable. After the mixture had been set aside for 2 h, HCl was removed under reduced pressure and the residue was distilled to give 2-*chloro*-4-*methyl*-1,3,2-*dithiaborolan* (24·4 g, 85%), b.p. 58°/6 mm., $n_D^{26}$ 1·5490 (Found: C, 23·95; H, 4·3; Cl, 22·55. $C_3H_6BClS_2$ requires C, 23·6; H, 3·95; Cl, 23·3%).

*Reaction between Dichlorophenylborane and Propane*-1,2-*dithiol*.—Propane-1,2-dithiol (2·86 g, 0·026 mol) was added slowly to dichlorophenylborane (4·21 g, 0·026 mol) at −78°. On removal of the HCl under reduced pressure the residue on distillation afforded 4-*methyl*-2-*phenyl*-1,3,2-*dithiaborolan* (4·40 g, 86%), b.p. 80°/0·1 mm, $n_D^{25}$ 1·6125 (Found: C, 55·65; H, 5·9. $C_9H_{11}BS_2$ requires C, 55·75; H, 5·65%).

*Reaction between* 2-*Chloro*-4-*methyl*-1,3,2-*dithiaborolan and Ethyl Lead Sulphide*.—Ethyl lead sulphide (7 g, 0·021 mol) was slowly added to a stirred benzene solution (30 ml) of 2-chloro-4-methyl-1,3,2-dithiaborolan (5·63 g, 0·038 mol); after the mixture had been heated under reflux for 2 h the lead salt was completely decolourised. The lead chloride was filtered off and after removal of the solvent under reduced pressure the residue on distillation afforded 2-*ethylthio*-4-*methyl*-1,3,2-*dithiaborolan* (5·23 g, 79·5%), b.p. 86°/3 mm, $n_D^{25}$ 1·5754 (Found: C, 34·7; H, 6·25. $C_5H_{11}BS_3$ requires C, 33·75; H, 6·2%).

*Reaction between* 2-*Chloro*-4-*methyl*-1,3,2-*dithiaborolan and Diethylamine*.—Diethylamine (8·66 g, 0·119 mol) was slowly added to a stirred solution of 2-chloro-4-methyl-1,3,2-dithiaborolan (6·01 g, 0·04 mol) in light petroleum at −78°. The mixture was allowed to reach room temperature and the insoluble diethylamine hydrochloride was filtered off. The solvent was removed under reduced pressure and the residue on distillation afforded 2-*diethylamino*-4-*methyl*-1,3,2-*dithiaborolan* (4·77 g, 64%), b.p. 87°/3·5 mm, $n_D^{25}$ 1·5228 (Found: C, 44·5; H, 8·6; N, 7·7. $C_7H_{16}BNS_2$ requires C, 44·5; H, 8·45; N, 7·4%).

*Reaction between* 2-*Diethylamino*-4-*methyl*-1,3,2-*dithiaborolan and Butylamine*.—Butylamine (0·375 g, 0·005 mol) was added to a benzene solution of 2-diethylamino-4-methyl-1,3,2-dithiaborolan (0·097 g, 0·006 mol) and the mixture was refluxed for 1 h. On removal of the volatiles, under reduced pressure, the residue on distillation afforded 2-*butylamino*-4-*methyl*-1,3,2-*dithiaborolan* (0·59 g, 61·5%), b.p. 86·7°/1·5 mm, $n_D^{27}$ 1·5229 (Found: C, 44·55; H, 8·7; N, 7·7. $C_7H_{16}BNS_2$ requires C, 44·5; H, 8·45; N, 7·4%).

*Reaction between* 2-*Chloro*-4-*methyl*-1,3,2-*dithiaborolan and* HCl.—Passage of HCl through a cooled light petroleum solution of 2-chloro-4-methyl-1,3,2-dithiaborolan resulted in recovery of starting material from the reaction mixture.

*Reaction between* 2-*Chloro*-4-*methyl*-1,3,2-*dithiaborolan and Butyl Alcohol*.—The reaction was found to be complex giving at least four boron-containing compounds none of which could be obtained in a pure form.

*Reaction between* 4-*Methylborolan*-2-*phenyl*-1,3,2-*dithiaborolan and Phenyl Isocyanate*.—Phenyl isocyanate (1·57 g, 0·016 mol) was added to a stirred ether–light petroleum (1 : 1) solution of 4-methyl-2-phenyl-1,3,2-dithiaborolan (1·28 g, 0·0065 mol). A white solid was formed overnight which was filtered off, washed with ether, and dried *in vacuo*; it was found to be the monoisocyanate complex (1·80 g, 87%), m.p. 130° (Found: C, 60·7; H, 5·3; N, 5·9. $C_{23}H_{21}BN_2O_2S_2$ requires C, 61·35; H, 5·1; N, 4·45%).

*Reaction between* 2-*Ethylthio*-4-*methyl*-1,3,2-*dithiaborolan and Phenyl Isocyanate*.—Phenyl isocyanate (0·91 g, 0·0076 mol) was added to a stirred ether–light petroleum (1 : 1) solution of 2-ethylthio-4-methyl-1,3,2-dithiaborolan (1·36 g, 0·0076 mol) at −70°. The solution was allowed to reach room temperature and was then refluxed for 3 h. Overnight a white solid formed which was filtered off, washed with ether, and on drying *in vacuo* it was found to be the isocyanate complex (1·33 g, 59%), m.p. 104—105° (Found: C, 47·2; H, 5·35; N, 4·7. $C_{12}H_{16}BNOS_3$ requires C, 48·5; H, 5·4; N, 4·7%).

*Reaction between* 2-*Diethylamino*-4-*methyl*-1,3,2-*dithiaborolan and Phenyl Isocyanate*.—Phenyl isocyanate (0·88 g, 0·007 mol) and 2-diethylamino-4-methyl-1,3,2-dithiaborolan (1·4 g, 0·007 mol) were allowed to react under the same conditions as those in the previous experiment. The isocyanate complex (0·78 g, 34%), m.p. 147 (Found: C, 55·4; H, 6·8. $C_{14}H_{21}BN_2OS_2$ requires C, 54·6; H, 6·8%) was obtained.

[2/2058 *Received*, 31*st August*, 1972]