SOME CYCLIC DERIVATIVES OF ETHYLENEDIAMINE CONTAINING SILICON, BORON, PHOSPHORUS, ARSENIC AND SULPHUR

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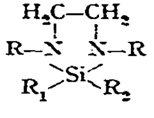
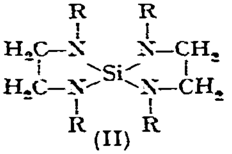
Attempts to produce silicon-containing heterocyclic systems from 1,2-diaminoethane have been reported to result only in the formation of polymeric products[1,2].



(I)



(II)

However, the presence of a single substituent upon each of the nitrogen atoms in 1,2-diaminoethane permits the isolation of cyclic compounds. Henglein and Lienhard[2] have obtained 1,2,2,3-tetramethyl-1,3-diaza-2-silacyclopentane (Ia, $R = R_1 = R_2 = Me$) from the transamination of bis(diethylamino)dimethylsilane with 1,2-bis(methylamino)ethane, and Kummer and Rochow[3] have obtained three compounds of type (I) from the dilithium salt of 1,2-bis(trimethylsilylamino)ethane: (Ib), $R = Me_3Si$, $R_1 = R_2 = Me$; (Ic), $R = Me_3Si$, $R_1 = Me$, $R_2 = Cl$; and (Id), $R = Me_3Si$, $R_1 = R_2 = Cl$.

In a further investigation of the reaction of 1,2-bis(methylamino)ethane with bis(diethylamino)dimethylsilane (eqn. 1), we have found that the five-membered ring compound, (Ia), reported previously[2], although perfectly stable in a high state of purity, polymerizes upon standing in the presence of certain impurities, in particular ammonium and alkylammonium salts. Polymerization is accompanied by a marked increase in refractive index and the rate may be followed at room temperature and at higher temperatures by this means. Addition of approx. 0.5 % of ammonium sulphate to a pure and completely stable sample of monomer brought about rapid polymerization which proceeded more rapidly at 50° than at room temperature. This gave a clear, highly viscous liquid with a measured molecular weight of 232. (Molecular weight of monomer is 132.) Heating the polymer at 200° results in thermal cracking, and a virtually complete recovery of the monomer by collection of the distillate*. It is likely that the polymerization proceeds by protonation of a nitrogen atom, followed by a nucleophilic attack at the silicon, in much the same way as the deamination and transamination reactions of aminosilanes under catalytic conditions[3a].

$$MeNH(CH_2)_2NHMe + Me_2Si(NEt_2)_2 \rightarrow 2Et_2NH + (MeNCH_2)_2SiMe_2 \qquad (1$$

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* The polymerisation process appears to be reversible even at room temperature. Monomer could be removed under reduced pressure from samples that had been allowed to polymerize for some time. After further standing, more monomer could be removed, indicating a depolymerisation toward an equilibrium mixture of monomer and polymers.

An analogous reaction between 1,2-bis(ethylamino)ethane and bis(diethylamino)dimethylsilane gave 1,3-diethyl-2,2-dimethyl-1,3-diaza-2-silacyclopentane (Ie, $R = Et$, $R_1 = R_2 = Me$) in high yield, but no polymerization was observed in this case. We thus observe an increase in the stability of the monomeric compounds, (I), as R goes from H to Me to Et.

The interaction of 1,2-bis(ethylamino)ethane and tetrakis(dimethylamino)silane has produced 2,2′-spirobis(1,3-diethyl-1,3-diaza-2-silacyclopentane) (IIa, $R = Et$) (eqn. 2).

$$2\ EtNH(CH_2)_2NHEt + Si(NMe_2)_4 \longrightarrow 4\ Me_2NH + (EtNCH_2)_4Si \qquad (2)$$

This compound is analogous* to the spiran (IIb, $R = Me_3Si$) recently obtained[3] from silicon tetrachloride and $Me_3SiNLi(CH_2)_2NLiSiMe_3$.

INFRARED SPECTRA

The infrared spectra of our monocyclic and spiran compounds have been recorded in the range 650–4000 cm^{-1}. The band at 930–950 cm^{-1} reported by Henglein and Lienhard[2], and tentatively assigned by them to the Si–N bond is also observed in our spectra of compounds (Ia), (Ie), and (IIa) at 926, 950 and 960 cm^{-1} respectively. A further band at about 1350 cm^{-1} has been assigned by Henglein to the five-membered ring system, and is also reported by Kummer and Rochow[3] for their compounds. This absorption is confirmed by us in the case of the N-methyl compound (Ia), but in (Ie) and (IIa) we find three sharp bands in this region, so that no definite assignment can be made. We note that the spectra of the monocyclic compound (Ie) is very similar to that of the spiran, except for the bands due to the $SiMe_2$ group at 1260 and 801 cm^{-1}.

PROTON MAGNETIC RESONANCE SPECTRA

Compounds of type (I) are the silicon analogues of the imidazolidines. Evidence has been given for geometrical isomerism in the latter compounds[4], and we have therefore investigated the possibility of the existence of *cis* and *trans* forms in our compounds. We find, however, that the resonances due to the ring CH_2 protons in the NMR spectra of compounds (Ia), (Ie) and (IIa) are in each case a single sharp peak. This indicates that the two faces of the five-membered rings are environmentally equivalent, and we thus confirm the findings of Baldeschwieler and Kummer[5] that the rings are planar and that either the nitrogen atoms are *sp*^{2}-hybridized, leading to a completely planar configuration about nitrogen, or, as seems more probable to the authors, inversion about nitrogen is sufficiently rapid to average the configurations. Details of the NMR spectra are recorded in Table 1.

REACTIONS WITH CERTAIN COVALENT HALIDES

Compounds containing silicon–nitrogen bonds are known to react with a variety of covalent halides, with elimination of a halosilane[6]. The interaction of 1,3-diethyl-2,2-

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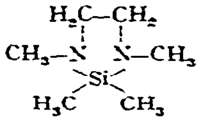
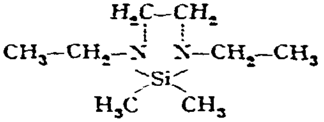
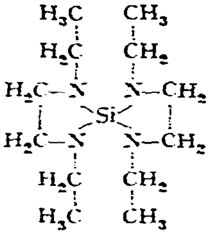
* Dr. J. J. ZUCKERMAN of Cornell University has recently informed us of his preparation of similar spirans of both silicon and germanium.

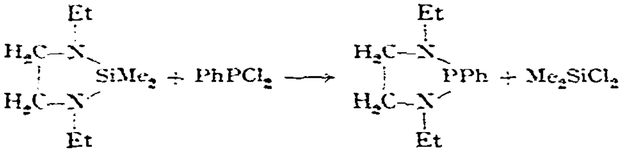
TABLE 1

PROTON CHEMICAL SHIFTS IN THE CYCLIC AND SPIRO SILICON–NITROGEN COMPOUNDS

Compound	*τ Values*	*Multiplicity*	*Assignment*
	10.00 7.53 7.11	Singlet Singlet Singlet	$C\underline{H}_3$–Si $C\underline{H}_3$–N $C\underline{H}_2$ in ring
	10.00 8.96 7.25 7.12	Singlet Triplet Singlet Quartet	$C\underline{H}_3$–Si $C\underline{H}_3$–CH_2–N $C\underline{H}_2$ in ring CH_3–$C\underline{H}_2$–N
	8.97 7.27 7.07	Triplet Quartet Singlet	$C\underline{H}_3$–CH_2–N CH_3–$C\underline{H}_2$–N $C\underline{H}_2$ in ring

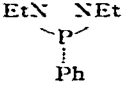
dimethyl-1,3-diaza-2-silacyclopentane with certain halides has therefore been investigated with a view to the formation of other heterocyclic compounds.

A typical reaction (with phenylphosphorus dichloride) is shown in eqn. 3.

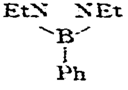


(3)

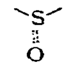
Phenylboron dichloride, arsenic trichloride, and thionyl chloride reacted similarly, and the heterocyclic products obtained are illustrated below: (III), (IV), (V), (VI).



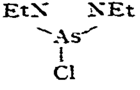
(III)



(IV)



(V)



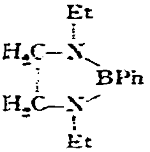
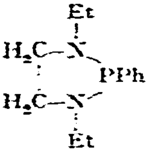
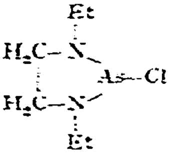
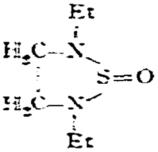
(VI)

1,3-Diethyl-2-phenyl-1,3-diaza-2-boracyclopentane (IV) has been reported previously[7], but we believe 1,3-diethyl-2-phenyl-1,3-diaza-2-phosphacyclopentane (III), 1,3-diethyl-2-oxo-1,3-diaza-2-thiacyclopentane (V) and 1,3-diethyl-2-chloro-1,3-diaza-2-arsacyclopentane (VI) to be examples of new heterocyclic systems.

The infrared spectra of these compounds have been recorded in the range 650 to 4000 cm^{-1}. The NMR spectra are also of interest, and the main features of these are reported in Table 2. The fine structures are now being investigated in greater detail, but certain features are immediately apparent at this stage.

TABLE 2

PROTON CHEMICAL SHIFTS IN THE BORON, PHOSPHORUS, ARSENIC AND SULPHUR HETEROCYCLIC COMPOUNDS

Compound	*τ Values*	*Multiplicity*	*Assignment*
	8.99 7.07 6.70 2.75	Triplet Quartet Singlet Singlet	$C\underline{H}_3$–CH_2–N CH_3–$C\underline{H}_2$–N $C\underline{H}_2$ in ring $C_6\underline{H}_5$–B
	8.84 7.14 7.10 2.40–3.0	Triplet Octet Doublet Complex multiplet	$C\underline{H}_3$–CH_2–N CH_3–$C\underline{H}_2$–N $C\underline{H}_2$ in ring $C_6\underline{H}_5$–P
	8.75 6.89 6.70	Triplet Quartet Singlet	$C\underline{H}_3$–CH_2–N CH_3–$C\underline{H}_2$–N $C\underline{H}_2$ in ring
	8.77 7.02 6.71	Triplet Octet Doublet	$C\underline{H}_3$–CH_2–N CH_3–$C\underline{H}_2$–N $C\underline{H}_2$ in ring

As might be expected, the values for the protons of the ring methylene groups are much more dependent upon the nature of the hetero atom than those of the substituent alkyl groups. In 1,3-diethyl-2-phenyl-1,3-diaza-2-boracyclopentane, the perfect singlet resonance for the ring methylene protons indicate either a planar ring or rapid inversion about the nitrogen atoms. In the phosphorus heterocycle, however, the proton resonance for the ring methylene groups and the ethyl methylene groups are split by the ^{31}P nucleus, giving a doublet and a double quartet respectively. In addition to this spin-spin coupling, further fine structure is present, apparently due to some configurational stability about the phosphorus atom with resultant chemical shifts of the protons involved. This effect has already been observed in the dioxaphospholanes[8], and we are investigating the spectrum of this compound further at different field strengths and temperatures. There also appears to be distinctive configurational stability about the sulphur atom in 1,3-diethyl-2-oxo-1,3-diaza-2-thiacyclopentane, resulting in non-equivalence of the protons above and below the ring, which appears as a splitting of both types of methylene proton present. The spectrum of 1,3-diethyl-2-chloro-1,3-diaza-2-arsacyclopentane is also being examined for evidence of configurational stability about arsenic.

EXPERIMENTAL

Preparations and techniques

All reactions were conducted under anhydrous conditions, and solvents and reagents were purified and dried before use. Bis(diethylamino)dimethylsilane, b.p. 36°/0.5 mm, n_D^{20} 1.4344, d_4^{16} 0.815, was prepared by the action of diethylamine on dichlorodimethylsilane in ether. In the preparation of tetrakis(dimethylamino)silane, the action of excess dimethylamine on silicon tetrachloride in ether gave, as the main product, chlorotris(dimethylamino)silane, which yielded the tertaaminosilane on treatment with the lithium salt of dimethylamine. Phenylboron dichloride was prepared as described by Gerrard and co-workers[9].

Infrared spectra were recorded with a Perkin Elmer Model 237 recording spectrophotometer, and NMR spectra in carbon tetrachloride solution with a Varian A60 instrument, using tetramethylsilane as an internal standard.

Interaction of 1,2-bis(methylamino)ethane and bis(diethylamino)dimethylsilane

The diamine (47.3 g, 1 mole) and the diaminosilane (108.7 g, 1 mole) were heated together with ammonium sulphate (~ 0.1 g), and diethylamine (69.0 g, 88 %), b.p. 56°, n_D^{20} 1.3840, was rapidly evolved. Subsequent distillation gave 1,2,2,3-tetramethyl-1,3-diaza-2-silacyclopentane (63.6 g, 82 %) b.p. 131–132°. Upon standing for two days the product became very viscous, but upon heating strongly (200°), and careful fractionation of the distillate, pure monomer, b.p. 131°, n_D^{20} 1.4350 (Found: C, 49.3; H, 11.2; N, 19.0. $C_6H_{16}N_2Si$ calcd.: C, 50.0; H, 11.1; N, 19.4%) was recovered virtually quantitatively. The refractive index of this pure monomer underwent no change on prolonged storage, and distilled smoothly without the need for elevated temperature.

Addition of about 0.5 % by weight of ammonium sulphate brought about polymerization of the purified monomer, as shown by the increase in refractive index. For a sample of which the refractive index had risen from 1.4350 to 1.4735 the molecular weight was found to be 232.

Interaction of 1,2-bis(ethylamino)ethane and bis(diethylamino)dimethylsilane

The diamine (15.26 g, 1 mole) and the aminosilane (26.58 g, 1 mole) were refluxed together with ammonium sulphate (~ 0.1 g) and diethylamine (17.75 g, 92.5 %) was immediately evolved, b.p. 56–8°, n_D^{21} 1.3838. Distillation of the residual liquid gave 1,3-diethyl-2,2-dimethyl-1,3-diaza-2-silacyclopentane (18.90 g, 84 %), b.p. 170°, n_D^{20} 1.4430. (Found: C, 55.08; H, 11.49; N, 15.7; mol. wt. ebullioscopic in acetone, 171.1. $C_8H_{20}N_2Si$ calcd.: C, 55.8; H, 11.65; N, 16.3 %; mol. wt., 172.)

Interaction of 1,2-bis(ethylamino)ethane and tetrakis(dimethylamino)silane

The diamine (8.65 g, 2 mole) and the aminosilane (7.60 g, 1 mole) were refluxed together with ammonium sulphate (~ 0.1 g) for 20 h, after which evolution of dimethylamine had ceased. Reduced pressure distillation of the resulting liquid gave, after a small forerun, 2,2'-spirobis(1,3-diethyl-1,3-diaza-2-silacyclopentane) (6.14 g, 65%), b.p. 112°/7 mm, n_D^{23} 1.4697. (Found: C, 55.43; H, 11.09; N, 21.2; mol. wt. ebullioscopic in acetone, 253.6. $C_{12}H_{28}N_4Si$ calcd.: C, 56.3; H, 10.92; N, 21.85 %; mol. wt., 256.)

Interaction of 1,3-diethyl-2,2-dimethyl-1,3-diaza-2-silacyclopentane with phenylboron dichloride

The dichloride (8.25 g, 1 mole) was added to the cyclic compound (8.93 g, 1 mole), dropwise at 0°. Heating the mixture caused evolution of dichlorodimethylsilane (5.55 g, 83 %), b.p. 70°, n_D^{26} 1.4008. Distillation of the remaining liquid gave 1,3-diethyl-2-phenyl-1,3-diaza-2-boracyclopentane (6.87 g, 65 %), b.p. 115°/8 mm, n_D^{19} 1.5229. (Found: C, 70.96; H, 9.21. $C_{12}H_{19}N_2B$ calcd.: C, 71.35; H, 9.42 %.)

Interaction of 1,3-diethyl-2,2-dimethyl-1,3-diaza-2-silacyclopentane and phenylphosphorus dichloride

The dichloride (9.07 g, 1 mole) and the cyclic compound (8.73 g, 1 mole) reacted in the same way as described for phenylboron dichloride above, giving dichlorodimethylsilane (5.90 g, 91 %), b.p. 70°, n_D^{23} 1.4062, and, after a considerable forerun (5 g), 1,3-diethyl-2-phenyl-1,3-diaza-2-phosphacyclopentane (4 g, 35 %), b.p. 98°/0.1 mm, n_D^{19} 1.5500. (Found: C, 63.7; H, 8.29; N, 12.8; mol. wt., 225. $C_{12}H_{19}N_2P$ calcd.: C, 64.9; H, 8.56; N, 12.6 %; mol. wt., 222.)

Interaction of 1,3-diethyl-2,2-dimethyl-1,3-diaza-2-silacyclopentane and thionyl chloride

Thionyl chloride (6.36 g, 1 mole) in toluene (10 ml) was added dropwise to the cyclic compound (9.20 g, 1 mole) in the same solvent (25 ml) at —78°. The solution became dark on reaching room temperature, and attempted distillation led to violent bumping. Volatile materials were therefore pumped off at 15 mm and trapped, leaving a brown oil. Distillation of the volatile products yields dichlorodimethylsilane (4 g, 58 %), b.p. 70–72°, n_D^{23} 1.4090, a large intermediate fraction, and toluene, b.p. 110°. Reduced pressure distillation of the brown residue gave 1,3-diethyl-2-oxo-1,3-diaza-2-thiacyclopentane (3.45 g, 40 %), b.p. 93–94°/4 mm, n_D^{23} 1.4843. (Found: C, 44.24; H, 8.39; N, 16.5; O, 9.89; S, 18.9; mol. wt., 162.5. $C_6H_{14}N_2SO$ calcd.: C, 44.45; H, 8.65; N, 17.3; O, 9.88; S, 19.75 %; mol. wt., 162.)

Interaction of 1,3-diethyl-2,2-dimethyl-1,3-diaza-2-silacyclopentane with arsenic trichloride

The trichloride (10.68 g, 1 mole) in toluene (7 ml) was added dropwise to the cyclic aminosilane (10.17 g, 1 mole) in toluene (30 ml) at 0°. The solution was refluxed for 6 h and dichlorodimethylsilane (5.75 g, 75 %), b.p. 70–73°, n_D^{20} 1.4090, was distilled out over a 3 h period. Removal of toluene at 20°/15 mm left a brown liquid, which yielded, on distillation, 1,3-diethyl-2-chloro-1,3-diaza-2-arsacyclopentane (5.5 g, 42 %), b.p. 86°/0.7 mm, n_D^{20} 1.5400. (Found: C, 31.9; H, 5.5; N, 11.7; mol. wt., 251.3. $C_6H_{14}N_2AsCl$ calcd.: C, 32.05; H, 6.23; N, 12.45 %; mol. wt., 224.5.)

Infrared spectra

Spectra were taken on thin liquid films, with sodium chloride optics. The absorption maxima were:

(Ia) 2950 sh, 2930 m, 2860 s, 2840 sh, 2793 s, 2705 vw, 2665 vw, 1469 m, 1442 w, 1365 vw, 1341 s, 1258 s, 1241 s, 1202 m, 1160 vs, 1120 vw, 1039 vs, 1019 sh, 926 s, 850 m, 808 s, 770 s, 720 w, 670 vw, 640 w.

(Ie) 2955 vs, 2920 sh, 2860 vs, 2800 vs, 2765 sh, 2740 sh, 2685 vw, 2640 vw, 1491 vw, 1480 vw, 1470 w, 1460 w, 1450 w, 1427 vw, 1391 w, 1374 m, 1349 m, 1330 m, 1305 sh, 1300 w, 1275 vw, 1250 vs, 1210 s, 1163 vs, 1120 m, 1090 w, 1075 sh, 1066 s, 1025 vw, 950 s, 930 sh, 860 sh, 843 m, 801 s, 772 vs, 718 m, 670 w, 649 w.

(IIa) 2958 vs, 2920 s, 2860 vs, 2805 vs, 2745 sh, 2700 w, 2682 w, 2640 w, 2580 vw, 2400 vw, 1480 sh, 1473 w, 1460 w, 1448 m, 1399 m, 1371 s, 1351 s, 1332 s, 1300 m, 1278 w, 1245 m, 1212 vs, 1205 sh, 1195 sh, 1168 vs, 1152 sh, 1130 sh, 1090 m, 1071 s, 1057 vs, 960 vs, 939 sh, 860 m, 788 w, 763 vs, 737 vw, 678 s.

(III) 3140 vw, 3060 m, 3045 m, 3020 w, 2998 sh, 2963 vs, 2927 s, 2885 s, 2863 s, 2827 vs, 2740 w, 2695 w, 2638 sh, 2580 sh, 2450 vw, 2330 vw, 1951 w, 1881 w, 1820 w, 1589 w, 1475 sh, 1463 sh, 1449 m, 1436 s, 1421 sh, 1380 s, 1359 m, 1323 w, 1292 w, 1250 w, 1232 w, 1200 s, 1178 vs, 1157 sh, 1150 vs, 1118 m, 1088 s, 1069 sh, 1040 s, 1029 sh, 998 m, 938 m, 910 w, 859 w, 820 vw, 791 w, 748 vs, 702 vs, 662 m, 635 m.

(IV) 3127 sh, 3100 sh, 3085 sh, 3052 s, 3022 sh, 3015 s, 2958 vs, 2930 vs, 2895 vs, 2870 sh, 2840 vs, 2740 sh, 2693 m, 2605 sh, 1952 w, 1883 w, 1820 w, 1770 w, 1606 m, 1552 sh, 1527 sh, 1511 sh, 1487 vs, 1463 sh, 1445 vs, 1430 vs, 1377 vs, 1358 vs, 1328 vs, 1267 vs, 1200 sh, 1182 s, 1157 sh, 1105 w, 1080 s, 1070 s, 1031 s, 980 vw, 949 w, 913 w, 895 w, 850 vw, 808 sh, 790 m, 750 vs, 703 vs, 668 sh, 650 sh, 638 s

(V) 2970 vs, 2935 vs, 2855 vs, 2760 sh, 2740 sh, 2690 vw, 1475 sh, 1468 s, 1450 s, 1437 sh, 1388 sh, 1380 s, 1357 m, 1321 m, 1300 sh, 1289 m, 1255 w, 1230 sh, 1200 sh, 1183 s, 1161 sh, 1128 sh, 1110 vs, 1100 sh, 1090 sh, 1078 sh, 1025 s, 1015 sh, 953 m, 915 m, 850 m, 803 sh, 792 w, 734 vw, 691 s, 685 sh.

(VI) 2962 vs, 2927 s, 2905 s, 2885 s, 2862 sh, 2840 vs, 2770 s, 2745 s, 2720 s, 2690 s, 2650 sh, 2575 w, 2503 w, 2475 m, 2458 m, 2380 m, 1475 s, 1460 s, 1397 s, 1383 s, 1360 s, 1332 m, 1309 m, 1280 w, 1263 m, 1247 w, 1213 s, 1190 sh, 1175 vs, 1150 vs, 1117 s, 1080 m, 1055 vs, 1045 sh, 1035 sh, 959 s, 947 s, 930 s, 851 s, 810 s, 800 sh, 625 s.

ACKNOWLEDGEMENTS

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SUMMARY

Interaction of 1,2-bis(alkylamino)ethanes with certain aminosilanes has given compounds containing the five-membered ring system 1,3-diaza-2-silacyclopentane. The reaction of 1,3-diethyl-2,2-dimethyl-1,3-diaza-2-silacyclopentane with phenylphosphorus dichloride, phenylboron dichloride, thionyl chloride and arsenic trichloride has given similar heterocycles containing phosphorus, boron, sulphur and arsenic at the 2-position. The infrared and NMR spectra of the compounds obtained have been recorded and discussed.

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