3. Fragmentation with rupture of the C—O bond in the alkyloxy group on the boron atom is characteristic for 2-alkoxy-1,2-azaborolines.

LITERATURE CITED

1. B. M. Zolotarev, O. S. Chizhov, A. S. Bleshinskaya, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 2226 (1979).
2. A. S. Bleshinskaya, B. M. Zolotarev, O. S. Chizhov, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 1566 (1980).
3. V. A. Dorokhov, O. G. Boldyreva, A. S. Shashkov, and B. M. Mikhailov, Izv. Akad. Nauk SSSR, Ser. Khim., 1431 (1976).
4. V. A. Dorokhov, O. G. Boldyreva, A. S. Shashkov, and B. M. Mikhailov, Heterocycles, 18, 87 (1982).
5. S. Meyerson, H. Hart, and L. C. Leitch, J. Am. Chem. Soc., 90, 3419 (1968).
6. S. Meyerson and E. Fields, Org. Mass Spectrom., 1, 263 (1968).
7. T. A. Elwood and M. M. Bursey, Org. Mass Spectrom., 1, 537 (1968).
8. R. S. Gohlke and F. W. McLafferty, Anal. Chem., 34, 1281 (1962).
9. G. H. Clark, R. Grigg, and D. H. Williams, J. Chem. Soc. B, 339 (1966).
10. A. A. Polyakova and R. A. Khmel'nitskii, Mass Spectrometry in Organic Chemistry [in Russian], Khimiya, Leningrad (1972), p. 76.
11. P. Powell, P. Sherood, M. Stephens, and E. F. H. Brittain, J. Chem. Soc. A, 2951 (1971).
12. W. G. Cole, D. H. Williams, and A. N. H. Yeo, J. Chem. Soc. B, 1284 (1968).

MASS SPECTROMETRIC STUDY OF 2-ORGANYLAMINO- AND 2-ORGANYLOXY-1-PROPYL-1,2-AZABOROLIDINES

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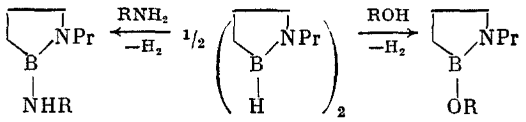
UDC 543.51:547.1'127

In continuation of studies on five-membered heterocycles of boron compounds by mass spectrometric methods [1], the behavior of 2-organylamino (I) and (II), and 2-organyloxy-1-propyl-1,2-azaborolidines (III)-(V) under electron impact is examined. Only 2-butoxy-1-benzyl-1,2-azaborolidine from this type of compounds has been synthesized earlier [2].

The dimer 2-n-propyl-1,2-azaborolidine served as the starting material for the synthesis of new organoboron compounds (I)-(V), from which by reaction with amines, (I) and (II) were obtained, and by reaction with alcohols and phenol, 2-alkoxy-1-propyl-1,2-azaborolidines (III) and (IV) and 2-phenoxy-1-propyl-1,2-azaborolidine (V) were obtained.



(I), (II) (III)—(V)

R = *t*-Bu (I), (IV), Ph (II), (V), *n*-Bu (III).

The structures of (I)-(V) were confirmed by data from physicochemical analytical methods. The IR spectra of (I) and (II) have characteristic intense bands between 3410-3420 cm^{-1} (N—H), and (III)-(V) between 1330-1370 cm^{-1} (B—O). 2-Organyloxy-1-propyl-1,2-azaborolidines are unstable in air, therefore a special method of probe insertion into the mass spectrometer was applied (see Experimental) for recording their mass spectra.

Peaks for the molecular ions $M^{+\cdot}$ are present in the mass spectra of (I)-(V), β-rupture of the N—Pr being the single general decomposition process, which was observed earlier for

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*Deceased.

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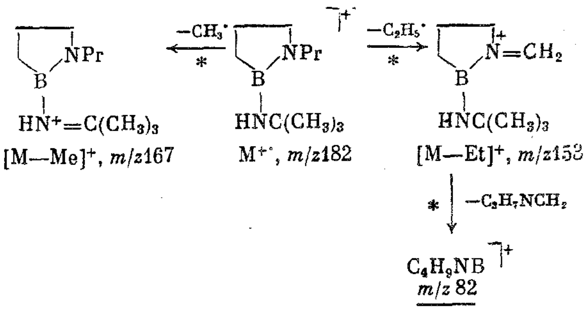
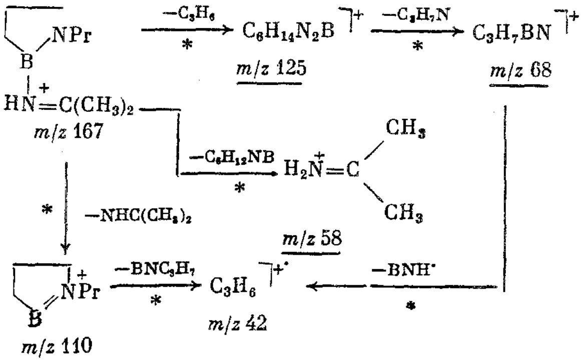
1,2-dialkyl-1,2-azaborolidines [1], with formation of the $[M-C_2H_5]^{+\cdot}$ ions. Their further decomposition depends on the nature of the R substituent. For example, $C_3H_7NCH_2$ is eliminated in (1) with formation of the $C_4H_9NB^+$ ion which can arise also directly from $M^{+\cdot}$ (Scheme 1).

Scheme 1†



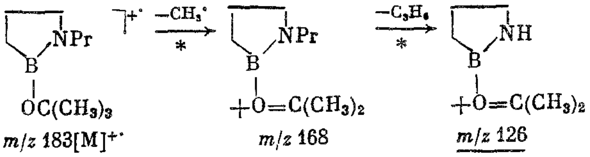
For (I), β-rupture of the tert-butyl group with elimination of a methyl radical (Scheme 1) is also characteristic. The $[M-Me]^+$ ion (m/z 167) which is formed decomposes by three paths (Scheme 2): 1) elimination of the boron-containing ring with transfer of a H atom to the immonium nitrogen leads to the ion with m/z 58, having maximal intensity in the mass spectrum of (I); 2) rupture of the B—N bond with subsequent destruction of the ring leads to the ions with m/z 110 and 42; and 3) elimination of C_3H_6 with formation of the $[C_6H_{14}N_2B]^+$ ion with m/z 125 and further decomposition to the ions with m/z 68 and 42. The second and third paths are analogous to those encountered in the decomposition of 2-dialkyl-1,2-azaborolidines [1].

Scheme 2



Loss of the $CH_3^{\cdot}$ radical from the t-Bu group with formation of the ion with m/z 168 and further the ion with m/z 126 (Scheme 3), as also occurs in the case of (1) (Scheme 2), is characteristic for 2-tert-butyl-1-propyl-1,2-azaborolidine [1]. In contrast to (I) and all earlier studied derivatives of 1,2-azaborolidines, the fragmentation of the $[M-C_2H_5]^+$ ion for 2-alkoxy-1-propyl-1,2-azaborolidines (III) and (IV) occurs with elimination of C_4H_8 from the alkoxy group on the boron atom with migration of a H atom to the oxygen atom (Scheme 4).

Scheme 3



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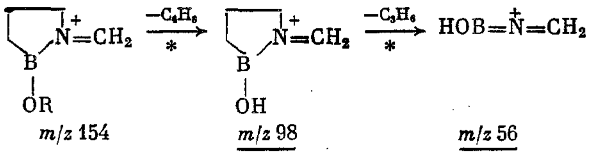
†Asterisks in the schemes denote decomposition paths confirmed by the corresponding metastable peaks; m/z of ions whose compositions were confirmed by exact mass measurements are underlined.

Scheme 4

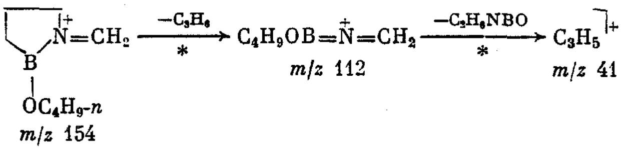


R = *n*-Bu, *t*-Bu.

This is the main process for 2-tert-butyl-1-propyl-1,2-azaborolidine (IV) (the ion with m/z 98 has maximal intensity in the mass spectrum of (IV)) and is less distinct for 2-n-butoxy-1-propyl-1,2-azaborolidine (III). Further fragmentation of the ion with m/z 98 proceeds with destruction of the ring and formation of the $[HOB{=}N{=}CH_2]^+$ ion with m/z 56.

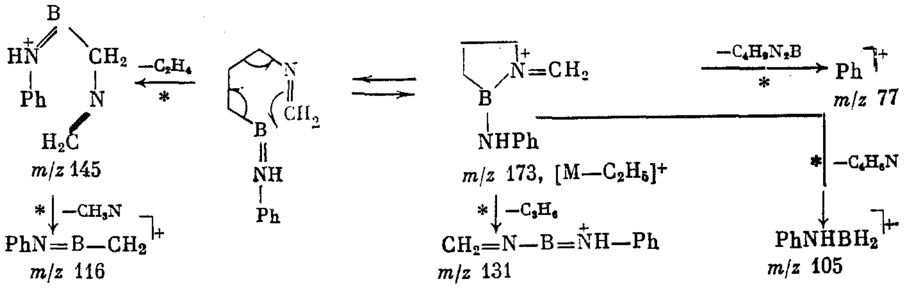
For 2-n-butoxy-1-propyl-1,2-azaborolidine (III) the main decomposition path in contrast to (IV) includes the destruction of the boron-containing ring and formation of the $C_3H_5^{+\cdot}$ ion (Scheme 5).

Scheme 5



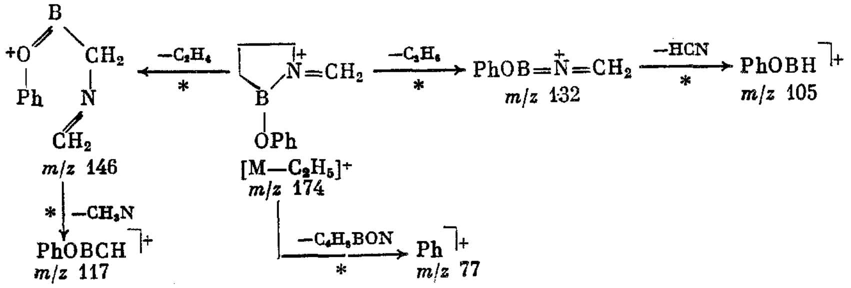
The intensity of the $C_3H_5^{+\cdot}$ ion is significantly lower in the mass spectrum of (IV) than in the mass spectrum of (III). In the case of 2-phenylamino-1-propyl-1,2-azaborolidine (II), a few decomposition paths for the $[M{-}C_2H_5]^+$ ion are possible with formation of the energetically favorable conjugated system (ions with m/z 116, 131, and 105, Scheme 6).

Scheme 6



The main decomposition path for 2-phenyloxy-1-propyl-1,2-azaborolidine (V) is also the formation of the $[M{-}C_2H_5]^+$ ion (m/z 174), further decomposition of which leads to the fragments $[PhOBNCH_2]^+$ (m/z 132), $[PhOBH]^+$ (m/z 105), $[PhOBCH]^+$ (m/z 117), and $[Ph]^+$ (m/z 77) (Scheme 7), similar to the decomposition of the analogous ion with m/z 173 in compound (II). A shift by one amu on going from (II) to 2-phenoxy derivatives of 1,2-azaborolidine (V) is confirmed by the fragmentation pattern of these compounds.

Scheme 7



From comparison of the mass spectra of compounds (I) and (II) with the mass spectra of their oxygen-containing analogs (IV) and (V) it follows that the presence of an oxygen atom on boron in (IV) and (V) leads to the appearance of a new possible fragmentation of the $[M{-}C_2H_5]^+$ ion with elimination of C_4H_8 from the butoxy group since the elimination process of the boron-containing ring with transfer of a H atom to the immonium nitrogen and formation of an

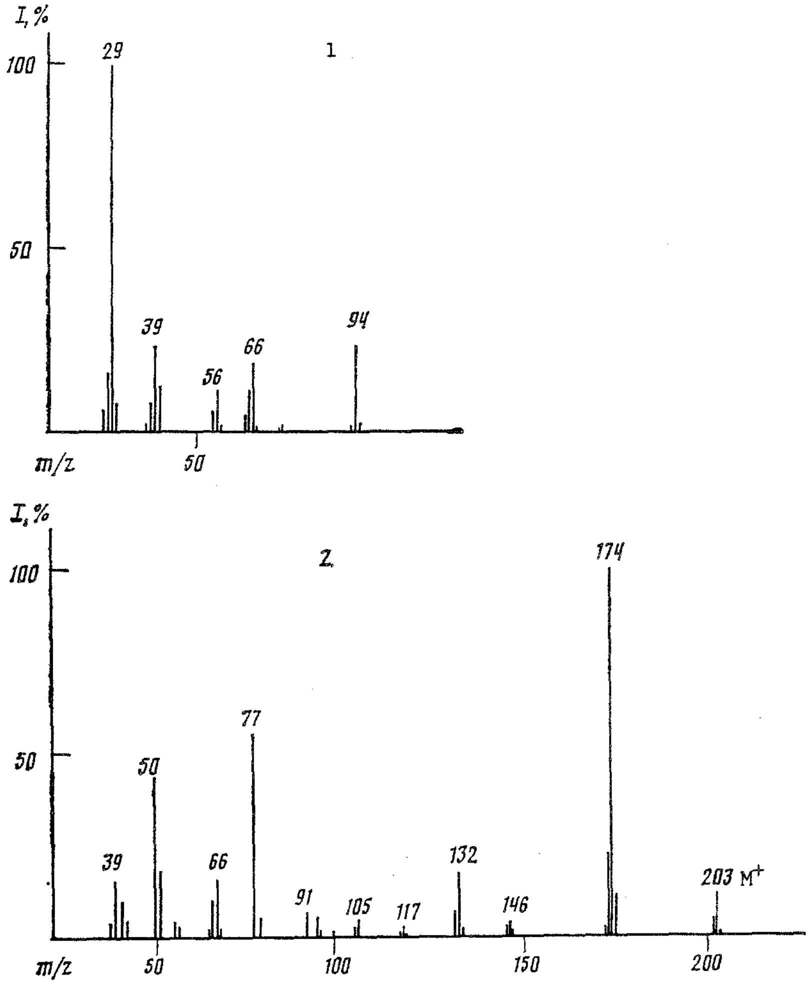


Fig. 1. Mass spectra of 2-phenoxy-1-propyl-1,2-azaborolidine (V) obtained by 1) the usual method; and 2) by application of the method for obtaining mass spectra of compounds which are unstable toward oxygen and moisture in air.

intense $[H_2N{=}C(CH_3)_2]^+$ ion (m/z 58) is characteristic for the compound with an alkylamine group on the boron atom (I). Thus, an alkylamino group on the boron atom stabilizes while an alkoxy group destabilizes the boron-containing ring and facilitates its destruction under electron impact.

The β-rupture of the N-propyl group, observed earlier for 1,2-dialkyl-1,2-azaborolidines [1], is a general decomposition process for all the compounds (I)-(V) studied.

EXPERIMENTAL

Mass spectra were obtained on a Varian MAT CH-6 mass spectrometer with direct sample insertion into the ion source. The ionization temperature of the chamber was 180°C, the electron ionization energy was 70 eV, and the emission current was 100 μA. The sample heating temperature was 26-60°C depending on volatility. High resolution mass spectra of compounds (I), (III), and (IV) were measured on a Varian MAT-311 mass spectrometer. The ionization chamber temperature was 200°C, the electron ionization energy was 70 eV, the emission current was 300 μA, and the inlet system temperature was ∿50°C.

Two methods were developed for obtaining mass spectra of compounds (III) and (IV), which hydrolyze in air: 1) The compound was sealed in a capillary, introduced into the direct inlet of the mass spectrometer and after evacuation of the system to 10^{-6} torr, the capillary was broken; 2) an argon-filled dry box, which was built of transparent polyethylene, was connected to an argon source and the direct inlet system of the mass spectrometer, and had gloves for manipulation of the compounds in the box, was used for solid compounds. Figure 1 shows the mass spectrum of compound (V), obtained by the usual method (1) and by the method recommended by us (2).

2-Tert-butylamino-1-propyl-1,2-azaborolidine (I). To a mixture of 4 g (0.018 mole) of 1-propyl-1,2-azaborolidine and 2.8 ml butylmercaptan heated to 120°C were added dropwise 2.6 g (0.035 mole) of tert-butylamine. The mixture was heated at the same temperature for 7 h until cessation of H_2 evolution (0.71 was released, GLC). Upon distillation, the yield of (I) was 2 g (31%), bp 96-98°C (5 mm), n_D^{20} 1.4562. Found: C 65.44; H 12.66; B 6.25; and N 15.65%. $C_{10}H_{23}BN_2$. Calculated: C 65.93; H 12.63; B 6.04; and N 15.38%. IR spectrum (CCl_4, ν, cm^{-1}): 3420 (N—H), 1520 (B—N). Mass spectrum, m/z (rel. intensity, %): 182(2) M^+, 181(0.6), 167(8), 166(2), 153(12), 152(3), 125(2), 110(2), 82(3), 81(1), 68(3), 59(4), 58(100), 57(3), 55(3), 42(16).

2-Phenylamino-1-propyl-1,2-azaborolidine (II) was synthesized analogously to (I). Yield, 4 g (69%) of (II), bp 168-170°C (3.5 mm), n_D^{20} 1.5480. Found: C 71.01; H 9.48; B 5.31; and N 14.20%. $C_{12}H_{19}BN$. Calculated: C 71.28; H 9.40; B 5.44; and N 13.86%. IR spectrum (CCl_4, ν, cm^{-1}): 3410 (N—H), 1522 (B—N). Mass spectrum, m/z (rel. intensity, %): 202(22) M^+, 201(8), 174(12), 173(100), 172(25), 171(7), 158(4), 157(4), 145(10), 144(7), 142(4), 132(4), 131(29), 130(10), 129(4), 128(8), 118(4), 117(5), 116(11), 115(5), 105(26), 104(14), 103(5), 94(5), 93(20), 92(4), 91(5), 78(6), 77(21), 76(4), 43(4), 42(5), 41(12), 39(16).

The synthesis of 2-organyloxy-1-propyl-1,2-azaborolidines (III)-(IV) was done by the general method: a mixture of 0.031 mole of 1-propyl-1,2-azaborolidine and 0.031 mole of absolute alcohol (or melted phenol) was heated at 150-170°C until cessation of H_2 evolution (GLC). The reaction products were purified by distillation.

2-n-butoxy-1-propyl-1,2-azaborolidine (III). Yield, 6.7 g (71%) of (III), bp 96-98°C (15 mm), n_D^{20} 1.4430. Found: C 65.39; H 12.17; and B 5.66%. $C_{10}H_{22}BNO$. Calculated: C 65.57; H 12.02; and B 6.01%. IR spectrum (CCl_4, ν, cm^{-1}): 1350 (B—O). PMR spectrum (CCl_4, δ, ppm): 3.41 m (OCH_2), 3.04 m (N—CH_2). Mass spectrum, m/z (rel. intensity, %): 183(1) M^+, 182(0.6), 154(21), 153(5), 119(8), 117(9), 112(14), 111(1), 98(13), 97(3), 57(9), 56(68), 55(17), 45(10), 43(58), 41(100), 39(30).

2-Tert-butoxy-1-propyl-1,2-azaborolidine (IV). Yield, 2.5 g (44%) of (IV), bp 102-103°C (21 mm), n_D^{20} 1.4283. Found: C 65.30; H 12.15; and B 5.73%. $C_{10}H_{22}BNO$. Calculated: C 65.57; H 12.02; and B 6.01%. IR spectrum (CCl_4, ν, cm^{-1}): 1347 (B—O), 1520 (B—N). PMR spectrum (CCl_4, δ, ppm): 2.65 m (N—CH_2), 1.03 s (CMe_3). Mass spectrum, m/z (rel. intensity, %): 183(3) M^+, 182(1), 168(3), 154(15), 153(4), 138(5), 137(2), 126(8), 125(3), 110(3), 109(0.3), 99(5), 98(100), 97(26), 96(5), 84(9), 83(3), 70(4), 69(5), 68(5), 59(30), 58(2), 57(15), 56(28), 55(12), 54(4), 53(5), 43(14), 42(16), 41(42), 39(15).

2-Phenoxy-1-propyl-1,2-azaborolidine (V). Yield, 3.8 g (60%) of (V), bp 125-126°C (10 mm), n_D^{20} 1.5191. Found: C 70.73; H 8.98; and B 5.02%. $C_{12}H_{18}BNO$. Calculated: C 70.93; H 8.86; and B 5.10%. IR spectrum (CCl_4, ν, cm^{-1}): 1340(B—O), 1490 (B—N). PMR spectrum (CCl_4, δ, ppm): 6.84 m (C_6H_5), 2.88 t (N—CH_2). Mass spectrum, m/z (rel. intensity, %): 203(12) M^+, 202(5), 175(12), 174(100), 173(23), 146(4), 132(18), 131(7), 117(3), 105(5), 104(3), 91(7), 87(3), 78(6), 77(56), 76(3), 68(3), 66(16), 65(11), 63(3), 56(4), 55(5), 51(19), 50(44), 43(4), 42(5), 41(10), 39(16).

CONCLUSIONS

1. The stability of the molecular ion and fragmentation of 2-organylamino- and 2-organyloxy-1-propyl-1,2-azaborolidines is determined by the nature of the R substituent in the NHR and OR groups on the boron atom. The main fragmentation process is β-rupture in the alkyl substituent on the endocyclic nitrogen atom.

2. Alkylamino groups on the boron atom stabilize the boron-containing ring. The alkoxy group destabilizes the boron-containing ring, facilitating its decomposition under electron impact.

3. A method is proposed for recording mass spectra of compounds unstable toward oxygen and moisture in air.

LITERATURE CITED

1. A. S. Bleshinskaya, B. M. Zolotarev, O. S. Chizhov, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 1566 (1980).
2. V. A. Dorokhov, O. G. Boldyreva, and B. M. Mikhailov, Zh. Obshch. Khim., 1528 (1970).