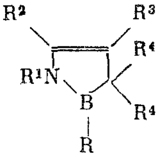
7. L. Ng, K. D. Jordan, A. Krebs, and W. Rüger, J. Am. Chem. Soc., 104, 7414 (1982).
8. V. I. Khvostenko, Mass Spectrometry of Negative Ions in Organic Chemistry [in Russian], Nauka, Moscow (1981), p. 59.
9. P. D. Burrow, A. Modelli, N. S. Chiu, and K. D. Jordan, Chem. Phys. Lett., 82, No. 2, 270 (1981).
10. D. Betteridge and M. Thompson, J. Mol. Struct., 21, 341 (1974).
11. Yu. A. Ustynyuk, Quantum Chemical Methods of Calculation [in Russian], Mosk. Gos. Univ., Moscow (1980).
12. R. Hoffman, Acc. Chem. Res., 4, 1 (1971).
13. C. N. R. Rao, P. K. Basu, and M. S. Hegde, Appl. Spectrosc. Rev., 15(1), 1-193 (1979).
14. V. A. Mazunov and V. I. Khvostenko, Prib. Tekh. Eksp., No. 4, 224 (1969).

ORGANOBORON COMPOUNDS AND MASS SPECTROMETRIC STUDY OF DERIVATIVES OF 2-AMINO- AND 2-OXY-1,2-AZABOROLINE

A. S. Bleshinskaya, O. G. Boldyreva,
B. M. Zolotarev, V. A. Dorokhov,
O. S. Chizhov, and B. M. Mikhailov*

UDC 543.51:547.1'127

In continuation of our work on the mass spectrometry of the simplest five-membered borazaheterocycles [1, 2], in this report the electron impact mass spectra of derivatives of 2-amino-1,2-azaboraline (I)-(X) [3, 4] are studied. The mass spectra of 2-organyloxy-1,2-azaborolines (XI)-(XIII) were also obtained for comparison. Compound (XII) was described in [4]; (XI) and (XIII) were synthesized by us by analogous methods.



R = NHBu-*t*, R^1 = Ph, R^2 = Ph, R^3 = H, R^4 = Bu-*n* (I);
R = NHPh, R^1 = Ph, R^2 = Ph, R^3 = H, R^4 = Bu-*n* (II);
R = NHBu-*n*, R^1 = Ph, $R^2 + R^3 = -(CH_2)_4-$, R^4 = Pr (III);
R = NHBu-*t*, R^1 = Ph, $R^2 + R^3 = -(CH_2)_4-$, R^4 = Bu-*n* (IV);
R = NHBu-*t*, R^1 = *m*-CH_3Ph, $R^2 + R^3 = -(CH_2)_4-$, R^4 = Pr (V);
R = NHBu-*t*, R^1 = *i*-Bu, $R^2 + R^3 = -(CH_2)_4-$, R^4 = Bu-*n* (VI);
R = NHBu-*t*, R^1 = *i*-Am, $R^2 + R^3 = -(CH_2)_4-$, R^4 = Bu-*n* (VII);
R = NHPh, R^1 = *i*-Bu, $R^2 + R^3 = -(CH_2)_4-$, R^4 = Bu-*n* (VIII);
R = NHPh, R^1 = Ph, $R^2 + R^3 = -(CH_2)_4-$, R^4 = Pr (IX);
R = NHPh, R^1 = Ph, $R^2 + R^3 = -(CH_2)_4-$, R^4 = Bu-*n* (X);
R = OBu-*n*, R^1 = Ph, $R^2 + R^3 = -(CH_2)_4-$, R^4 = Pr (XI);
R = OC_6H_{13}, R^1 = Ph, $R^2 + R^3 = -(CH_2)_4-$, R^4 = Bu-*n* (XII);
R = OPh, R^1 = Ph, $R^2 + R^3 = -(CH_2)_4-$, R^4 = Pr (XIII).

Mass spectra of these compounds contain intense molecular ion peaks, $M^{+\cdot}$ (10-30% of the intensity of the base peak). The general fragmentation process for them is the elimination of an alkyl radical and a molecule of olefin from the R^4 substituent with formation of $[M-R^4]^+$ ions (with maximal intensity in the mass spectra of these compounds) and $[M-(R^4-CH_2)]^+$ respectively. The remaining peaks are small by comparison. Further decomposition of these ions leads to the $[(M-R^4)-(R^4-CH_2)]^+$ ions, similar to the formation process of tropylium ions from alkylbenzenes [5].

---

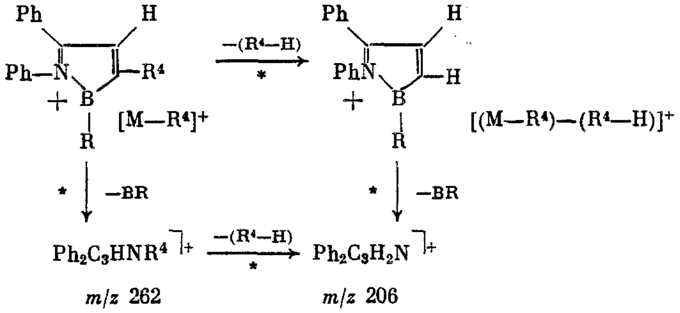
*Deceased.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 587-593, March 1989. Original article submitted November 5, 1987.

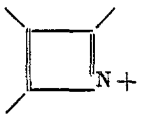
0568-5230/89/3803-0517$12.50

Besides the general path, specific fragmentation paths are also observed depending on the nature of the substituents R, R^1, R^2, and R^3. Thus, the elimination of BR particles from the $(M-R^4)^+$ and $[(M-R^4)-(R^4-H)]^+$ ions is characteristic for (I) and (II) with destruction of the boron-containing ring and formation of the $[Ph_2C_3HNR^4]^+$ (m/z 262) and $[Ph_2C_3H_2N]^+$ (m/z 206) ions. The latter is also formed from the $[Ph_2C_3HNR^4]^+$ ion through elimination of the (R^4-H) particle (Scheme 1).

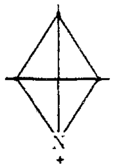
Scheme 1



The $-C_3HN-$ fragment in the ions with m/z 206 and 262 can have the azacyclobutadiene (A) or azatetrahedrane (B) structure, analogous to those which have been described for similar ions formed from some carbo- and heterocyclic systems [6-9].



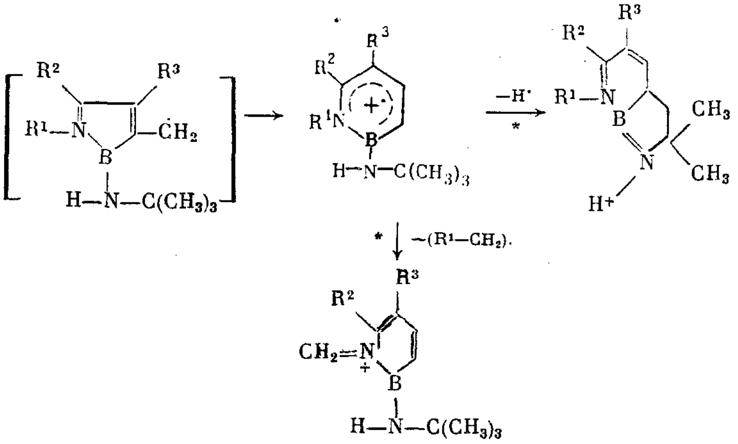
(A)



(B)

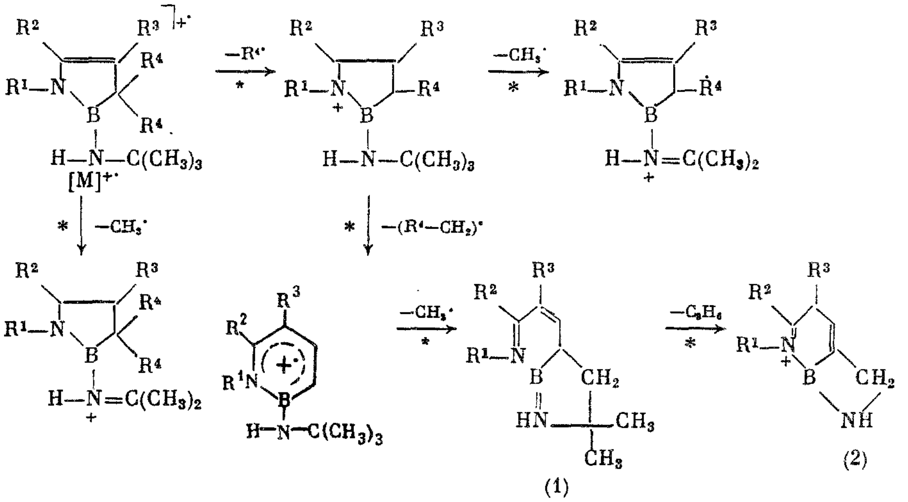
In contrast to (I) and (II), further decomposition of the $[(M-R^4)-R^4-CH_2)]^{+\cdot}$ ions for (III)-(X) proceeds with elimination of $H^\cdot$ and leads to more stable ions (increase in intensity of the corresponding peaks in the mass spectra) (Scheme 2). Rearrangements of this type are known for phenyl- and benzylindoles, phenyltryptamines [10], and tri-N-alkylborazoles [11].

Scheme 2



The presence of an alkyl group on the nitrogen atom (R^1 = Alk) in the ring (VI)-(VIII) leads to the possibility of decomposition of the $[(M-R^4)-(R^4-CH_2)]^{+\cdot}$ ion through β-rupture of the C—C alkyl bond and elimination of the (R^1-CH_2) particle (Scheme 2). For (IV)-(VII) (R = NHBu-t), β-rupture relative to the nitrogen atom in the t-Bu group with elimination of a $CH_3^\cdot$ radical is characteristic (Scheme 3).

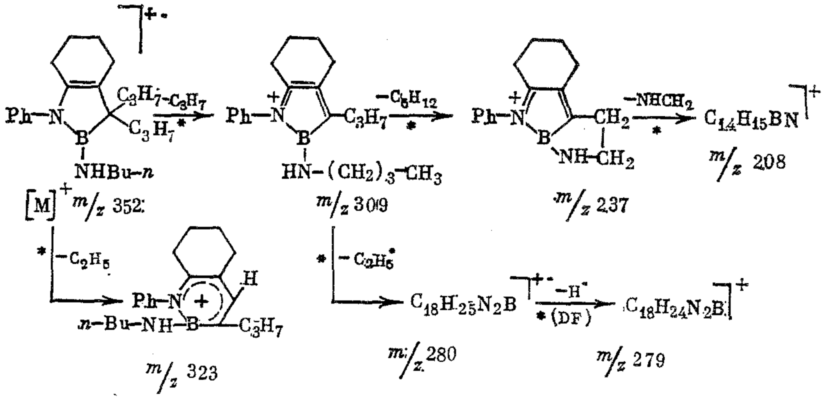
Scheme 3



Further fragmentation of the ion (1) occurs with elimination of C_3H_6 and formation of the ion (2). The composition of ions (1) and (2) was confirmed by measurement of their exact mass.

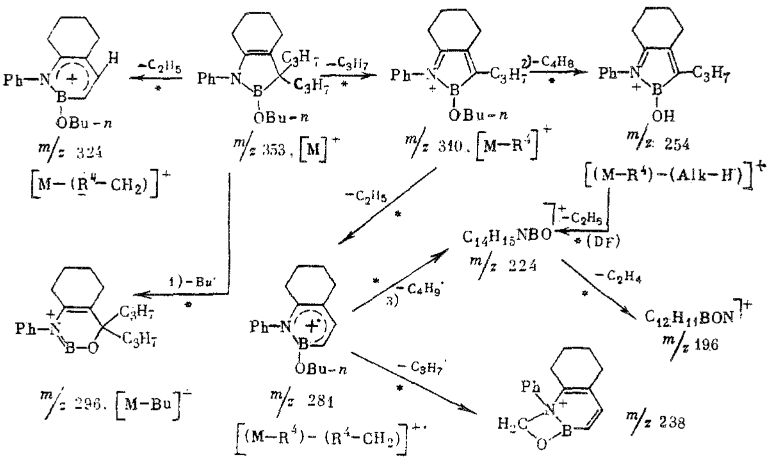
Fragmentation of (III) (R = NHBu-n) is shown in Scheme 4, which was confirmed by defocusing (DF) and measurement of the exact mass of the ions formed with m/z 280, 279, 237, and 208.

Scheme 4



Introduction of an alkoxy group on the boron atom (XI)-(XII) does not change the basic processes of fragmentation, but leads to an additional decomposition mode (1-3), given in Scheme 5. The fragmentation of $M^{+\cdot}$ with rupture of the C–O bond and elimination of the alkyl substituent as a radical is characteristic for (XI) and (XII) (Scheme 5, path 1). The fragmentation of the $(M-R^4)^+$ ion occurs with elimination of alkene from the R substituent on the boron atom and the migration of the boron atom to oxygen (path 2).

Scheme 5



Further decomposition of the ion which is formed $[(M-R^4)-(Alk-H)]^+$, leads to an ion with m/z 224 upon elimination of C_2H_6 (or C_3H_8) from R^4. The ion with m/z 224 is also formed upon fragmentation of the $[(M-R^4)-(R^4-CH_2)]^{+\cdot}$ ion with elimination of the alkyl radical from the oxygen atom (path 3). Decomposition of the ion with m/z 224 leads further to the ion with composition $[C_{12}H_{11}NBO]^+$ with m/z 196 as a result of loss of C_2H_4 (both the path of formation for the ion with m/z 224 and its further decomposition were confirmed by DF). The composition of the ions with m/z 224 and 196 were established by measurement of their exact masses as for compound (XII). The ion $[(M-R^4)-(R^4-CH_2)]^{+\cdot}$ can also be decomposed with loss of $(Alk-CH_2)^\cdot$ radical from the alkoxy group with formation of an ion with m/z 238. The analogous process is known for α-alkyl and α-alkoxypyridines [12].

The presence of a Ph group as a substituent on either of the nitrogen atoms in 2-organylamino-1,2-azaborolines (II)-(V), (VIII)-(X) leads to the appearance of characteristic peaks at m/z 77 $(Ph)^+$ and 91 $(C_7H_7)^+$, which are a result of skeletal rearrangement of the ion with m/z 105 $(C_8H_9)^{+\cdot}$.

Rearrangement of the $[C_{18}H_{16}N_2B]^+$ (m/z 271) ion, formed upon fragmentation of the $[(M-R^4)-(R^4-CH_2)]^{+\cdot}$(m/z 300) ion with loss of a $C_2H_5^\cdot$ radical from the cyclohexenyl ring adjacent to the boron-containing heterocycle (confirmed by DF and exact mass measurement of the ion with m/z 271 for compound (X)), is characteristic in the mass spectra of compounds with phenyl substituents on both nitrogen atoms, (IX) and (X), in contrast to 2-alkylamino derivatives of 1,2-azaboroline.

The presence of such rearrangements for ions (m/z 300 and 271) and the corresponding metastable ions in the mass spectrum (XIII) confirms the fact that the ion with m/z 271 apparently is formed as a result of destruction of the cyclohexenyl ring which is condensed with the boron-containing ring.

The behavior of compound (XIII) (R = PhO) under electron impact differs somewhat from that of (XI) and (XII). For (XIII), decomposition with formation of the $[(M-R^4)-(R-H)]^+$ ion is impossible (Scheme 5). Fragmentation of the $[(M-R^4)-(R^4-CH_2)]^{+\cdot}$ ion with elimination of $Ph^\cdot$ from the boron atom and formation of the ion with m/z 224 also is unlikely since $Ph^\cdot$ is less stable by comparison with $Alk^\cdot$. In the mass spectrum of (XIII), the ion with m/z 238 also is not observed since the loss of $(Ph-CH_2)^\cdot$ is not possible. For (XIII), the increase in intensity of the Ph^+ ion is characteristic.

As seen from the material given above, the decomposition of the derivatives of 1,2-azaboroline studied, (I)-(XIII), proceed selectively under electron impact: in the mass spectra of all compounds the peak for the ion $[M-R^4]^+$ has the maximal intensity, the remaining ions are significantly less in intensity. Together with the presence of sufficiently stable molecular ions, this feature simplifies the mass spectrometric identification of the indicated compounds.

EXPERIMENTAL

Mass spectra were obtained on a Varian MAT CH-6 mass spectrometer with direct sample introduction in the ion source. The ionization temperature in the chamber was 180°C, the electron ionization energy was 70 eV, and the emission current was 100 μA. The sample heating temperature was varied between 25-60°C depending on the volatility.

High resolution mass spectra of heterocycles (III), (V), (X), and (XII) were measured on a Varian MAT 311A mass spectrometer. The ionization temperature in the chamber was 200°C, the electron ionization energy was 70 eV, the emission current was 300 μA, and the temperature of the inlet system was ∿50°C.

2-Organylamino-1,2-azaborolines (I)-(X) were obtained according to [3, 4]. Synthesis of 2-hexyloxy-1-phenyl-3,3-dibutyl-4,5-tetramethylene-1,2-azaboroline (XII) was described in [4].

2-Butoxy-1-phenyl-3,3-dipropyl-4,5-tetramethylene-1,2-azaboroline (XI). To 10.8 g 2-phenylamino-1-phenyl-3,3-dipropyl-4,5-tetramethylene-1,2-azaboroline (IX) in 15 ml absolute C_4H_9OH was added in portions a solution of 0.029 mole of HCl in abs. C_4H_9OH. The precipitate of aniline hydrochloride was filtered and washed with hexane. The filtrate was evaporated. Vacuum distillation of the residue gave 4.6 g (45%) of compound (XI) with bp 146°C (0.8 mm), n_D^{20} 1.5120. Found: C 78.19; H 10.28; B 3.14; and N 4.02%. $C_{23}H_{36}BNO$. Calculated: C 78.18; H 10.27; B 3.07; and N 3.96%. IR spectrum (in CCl_4, ν, cm^{-1}): 1340-1370 (B-O), 1670 (C=C). PMR spectrum (in CCl_4, δ, ppm): 4.27 t (OCH).

2-Phenoxy-1-phenyl-3,3-dipropyl-4,5-tetramethylene-1,2-azaboroline (XIII). A mixture of 4.2 g 2-butoxy-1-phenyl-3,3-dipropyl-4,5-tetramethylene-1,2-azaboroline (XI) and 1.5 ml melted phenol were heated at 150-170°C in vacuum (40-50 torr). One ml of C_4H_9OH were given off. Distillation of the residue gave 3.4 g (76%) of compound (XIII), bp 155-157°C (0.8 mm), n_D^{20} 1.5010. Found: C 80.28; H 8.83; B 2.92; and N 4.20%. $C_{25}H_{32}BNO$. Calculated: C 80.42; H 8.64; B 2.90; and N 3.75%. IR spectrum (in CCl_4, ν, cm^{-1}): 1330-1370 (B—O), 1670 (C=C). PMR spectrum (in CCl_4, δ, ppm): 7.23-6.50 m (Ph), multiplet at 4.27 ppm (OCH_2) is absent.

Mass spectra (m/z (intensity, %)): ions with intensity <5% (except molecular and those near it, and also those mentioned in the discussion) are excluded.

(I). Mol. wt. 402. 402(8), 401(2), 359(2), 346(26), 345(100), 344(19), 330(2), 302(2), 302(2), 289(10), 287(11), 262(6), 261(2), 246(7), 245(6), 206(19), 205(5), 104(7), 103(5), 91(6), 77(10).

(II). Mol. wt. 422. 422(12), 421(4), 379(2), 366(31), 365(100), 364(22), 323(8), 322(11), 321(12), 309(12), 308(3), 263(8), 262(11), 261(4), 207(6), 206(41), 205(9), 196(6), 195(8), 192(14), 180(14), 128(9), 115(5), 104(11), 103(8), 93(23), 92(5), 91(9), 78(6), 77(47).

(III). Mol. wt. 352. 352(18), 351(6), 323(1), 310(26), 309(100), 308(25), 280(4), 279(6), 267(6), 265(5), 251(7), 237(20), 236(5), 223(6), 209(5), 208(6), 181(2), 180(3), 133(2), 130(4), 129(3), 119(3), 118(4), 117(3), 105(4), 104(5), 103(3), 93(3), 92(2), 91(7), 81(3), 79(5), 78(3), 77(7), 67(4), 57(3), 55(6), 43(16), 42(7), 41(18), 39(5).

(IV). Mol. wt. 380. 380(10), 379(3), 365(1), 337(1), 324(23), 323(100), 322(23), 308(1), 280(1), 279(2), 265(7), 264(2), 223(2), 208(1), 195(4), 93(1), 77(2), 58(2), 57(3), 41(4).

(V). Mol. wt. 366. 366(16), 365(5), 351(1), 337(1), 324(4), 323(100), 322(21), 308(0.8), 294(1), 293(2), 281(1), 279(7), 278(2), 268(4), 237(3), 223(2), 195(2), 194(1), 133(5), 105(1), 93(1), 79(1), 77(1).

(VI). Mol. wt. 360. 360(13), 359(5), 345(1), 317(3), 316(1), 304(22), 303(100), 302(21), 288(1), 275(1), 260(2), 259(3), 248(1), 247(4), 246(2), 245(5), 244(1), 217(5), 216(1), 203(3), 202(1), 161(7), 160(3), 118(2), 57(6), 41(9).

(VII). Mol. wt. 374. 374(13), 373(5), 359(1), 331(1), 318(21), 317(100), 316(23), 302(1), 274(1), 273(2), 261(3), 260(2), 259(3), 232(2), 217(4), 216(1), 161(3), 123(2), 157(3), 43(3).

(VIII). Mol. wt. 380. 390(14), 379(4), 337(3), 336(1), 324(25), 323(100), 322(19), 280(4), 279(5), 267(6), 266(9), 237(13), 236(4), 223(4), 220(3), 195(4), 128(4), 105(4), 104(2), 93(5), 91(3), 77(3).

(IX). Mol. wt. 372. 372(27), 371(8), 343(1), 330(25), 329(100), 328(24), 301(3), 300(8), 299(9), 287(3), 286(1), 272(3), 271(7), 208(3), 166(8), 165(3), 150(6), 93(5), 91(2), 77(5).

(X). Mol. wt. 400. 400(21), 399(6), 357(1), 344(25), 343(100), 342(22), 301(4), 300(9), 299(9), 298(2), 287(3), 286(1), 272(9), 271(9), 270(2), 195(2), 105(1), 104(2), 93(3), 91(3), 77(3).

(XI). Mol. wt. 353. 353(16), 352(4), 324(2), 311(23), 310(100), 296(3), 281(6), 280(1), 254(8), 253(3), 238(4), 224(8), 223(3), 196(9), 195(4), 105(5), 91(8), 79(6), 77(13), 41(19).

(XII). Mol. wt. 409. 409(12), 408(4), 366(3), 365(1), 353(26), 352(100), 351(22), 324(1), 309(4), 296(4), 295(2), 269(4), 268(16), 267(5), 239(2), 238(6), 237(2), 224(12), 223(4), 212(8), 196(13), 195(6), 119(4), 105(4), 91(6), 77(6), 43(25), 41(18).

(XIII). Mol. wt. 373. 373(48), 372(17), 344(7), 343(2), 331(23), 330(100), 329(19), 301(12), 300(8), 288(15), 287(6), 272(8), 271(3), 254(12), 253(4), 105(6), 104(3), 93(4), 91(11), 77(51), 51(7), 43(10).

CONCLUSIONS

1. Decomposition under the influence of electron impact of 2-organyl-1,2-azaborolines (I)-(XIII) occurs selectively, in the mass spectra an intense peak of the $[M-R^4]^+$ ion dominates, explained by the loss of the substituent from C^3, the remaining ions usually do not exceed 10% of its intensity.

2. The boron-containing ring in the bicyclic compounds (III)-(XIII) is more stable to the influence of electron impact.

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).

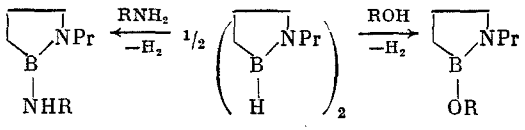
MASS SPECTROMETRIC STUDY OF 2-ORGANYLAMINO- AND 2-ORGANYLOXY-1-PROPYL-1,2-AZABOROLIDINES

A. S. Bleshinskaya, O. S. Chizhov,
B. M. Zolotarev, B. M. Mikhailov,*
and V. A. Dorokhov

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

---

*Deceased.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow.
Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 593-598, March 1989. Original article submitted November 5, 1987.

0568-5230/89/3803-0522$12.50