Heteroatom Chemistry
Volume 8, Number 5, 1997

The Mass Spectra of 1- and 2-Alkylbenzotriazoles

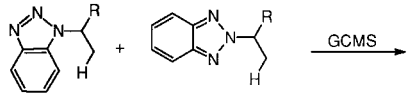
Alan R. Katritzky,* Isolde B. Puschmann, David H. Powell, and Adam P. Wells

Center for Heterocyclic Compounds, Department of Chemistry, University of Florida, Gainesville, FL 32611-7200

Received 6 December 1996; revised 25 May 1997

ABSTRACT

The fragmentation patterns of a series of 1- and 2-alkylbenzotriazoles are recorded and interpreted in comparison with available literature data. 1- and 2-Substituted benzotriazoles are readily differentiated on the basis of the relative ease with which a 1-substituted isomer loses nitrogen compared with the corresponding 2-isomer, resulting in generally weak parent ions for the former and strong parent ions for the latter. This loss of nitrogen in the 1-isomer ultimately gives rise to a strong peak at m/z 104, which is small or absent in the 2-isomer. In addition, examination of the intensity and distribution of peaks clustered around m/z 118 reveals that weak signals with a maximum intensity at m/z 117 or 118 are indicative of the 1-isomers, while strong signals with a maximum intensity at 119 or 120 are typical of the 2-isomers.



Thus, isomers are distinguished by analysis of mass spectral cracking patterns. © *1997 John Wiley & Sons, Inc. Heteroatom Chem.* 8*: 459–464, 1997*

Submitted in honor of the seventy-fifth birthday of Bill McEwen, a fine chemist and a long-time friend.—A. R. K.

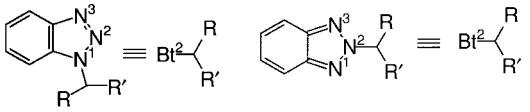
*To whom correspondence should be addressed.

 CCC 1042-7163/97/050459-06

INTRODUCTION

In connection with extensive synthetic work involving 1- and 2- substituted benzotriazoles [1,2], we have used the technique of mass spectroscopy to distinguish between these isomers (Scheme 1).

Although there has been extensive work on the mass spectrometry of heterocyclic compounds [3] and significant work on the fragmentation patterns of some benzotriazoles has appeared in the literature [4,8], no comprehensive study of the latter has been published. We now report the mass spectra of a substantial number of 1- (**1**) and 2-alkylbenzotriazoles (**2**) and attempt to rationalize their fragmentation



1 **2**

a	R = n-C_3H_7	R′ = n-C_4H_9	N-octylbenzotriazole
b	R = CH_3	R′ = n-C_3H_7	N-pentylbenzotriazole
c	R = C_2H_5	R′ = C_2H_5	
d	R = CH_3	R′ = n-C_6H_{13}	N-octylbenzotriazole
e	R = C_2H_5	R′ = C_5H_9	
f	R = CH_3	R′ = n-C_8H_{17}	N-decylbenzotriazole
g	R = C_2H_5	R′ = n-C_7H_{15}	
h	R = n-C_3H_7	R′ = n-C_6H_{13}	
i	R = n-C_4H_9	R′ = n-C_5H_{11}	
j	R = Ph	R′ = n-C_3H_7	N-(1-phenylbutyl)triazole
k	R = $PhCH_2$	R′ = C_2H_5	
l	R = $PhCH_2CH_2$	R′ = CH_3	

SCHEME 1

patterns in comparison with those already published.

RESULTS

The positive ion mass spectra of a number of isomeric *N*-alkylbenzotriazoles were recorded using electron ionization (EI) at 70 eV.

The mass spectrum of 4-(benzotriazol-1-yl)octane (**1a**) shown in Figure 1 is typical of most 1-alkylbenzotriazoles. *N*-Alkylbenzotriazoles are fairly robust under conditions of EI, since a parent ion (M^+) of at least moderate intensity is always observed. As may be expected of a substituted alkane, the next most massive ions result from cleavage of the alkyl chain, giving rise to small peaks at *m/z* 216 and *m/z* 202, due to loss of CH_3 and C_2H_5, respectively. Also typical of alkyl-substituted amines, significant α-fragmentation occurs on either side of the point of attachment of the benzotriazolyl (Bt) group, to give ions corresponding to M minus propyl (*m/z* 188) and M minus butyl (*m/z* 174). The next most significant cleavages involve the loss of N_2 from each of these ions to give strong peaks at *m/z* 160 and 146, respectively. Loss of the remaining alkyl side chain from either of these ions gives rise to the base peak at *m/z* 104, which can fragment further by loss of HCN to form an ion of *m/z* 77. The ion of *m/z* 132 could result from the loss of part of an alkyl side chain from any of the higher mass ions. High-resolution MS has shown that the cluster of ions around *m/z* 119 is *not* due to simple elimination of benzotriazole (BtH) from the alkyl chain. These ions are due to a species with the formula C_8H_xN, where x = 7, 8, 9, and 10 (for *m/z* 117, 118, 119, and 120, respectively) and range from weak to strong intensity.

The mode of fragmentation for very simple, terminally substituted 1- and 2-alkylbenzotriazoles (where alkyl = methyl, ethyl, and deuteroethyl) have been reported by Maquestiau and co-workers [4]. While the mass spectra of these simple compounds are significantly different from the nonterminal, long-chain alkyl-benzotriazoles used in the current study, modified versions of some of Maquestiau's proposed mechanisms can account for the major peaks observed in the mass spectra.

The general fragmentation scheme for 1-(secondary-alkyl)benzotriazoles (**1**; R, R′ ≠ H), in which the Bt group is not located on position 1 of the alkyl chain, is given in Figure 2. Maquestiau et al. [4] observed loss of N_2 as an important fragmentation pathway in 1-methyl- and 1-ethyl-benzotriazole, and our spectra of these compounds closely match those reported. However, we observed the loss of N_2H and/or C_2H_5 in all cases where the attached alkyl chain contained more than three carbons, as determined by spectra obtained under high-resolution conditions ($m/\Delta m$ = 8000). Lawrence and co-workers [6] have also observed this fragmentation in 1-benzyl-

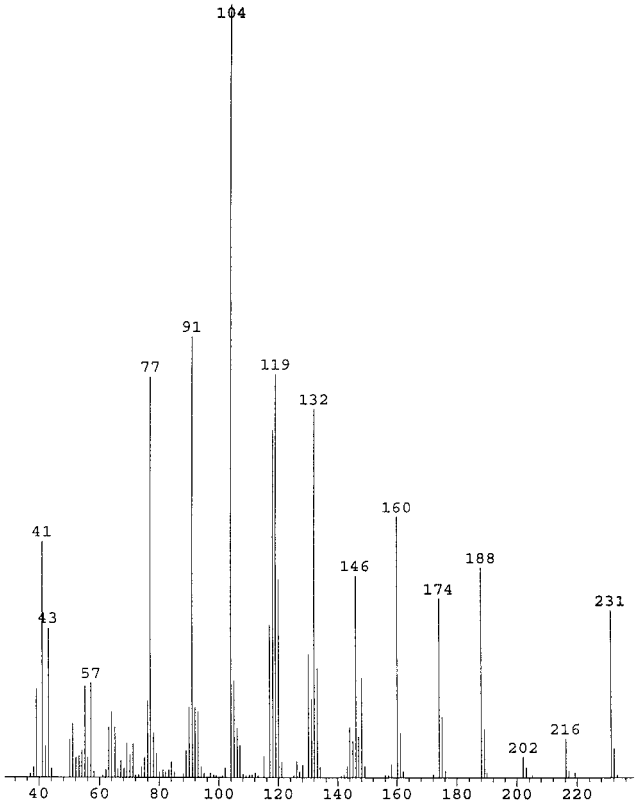


FIGURE 1 EI mass spectrum of 4-(benzotriazol-1-yl)octane.

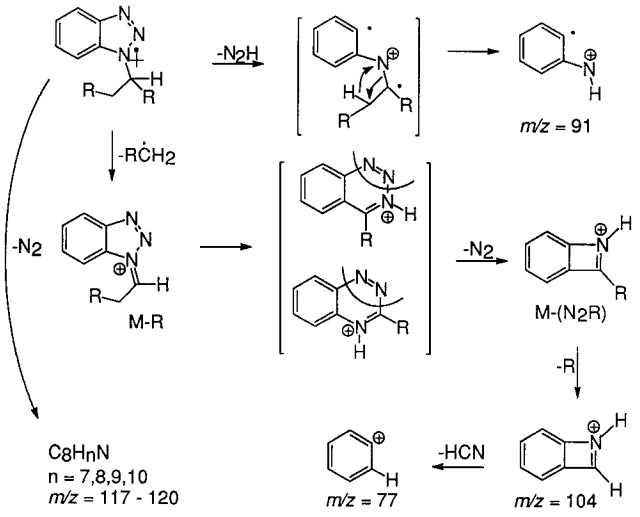


FIGURE 2 General fragmentation scheme for 1-alkylbenzotriazoles.

benzotriazole and determined that the loss of N_2H was not the stepwise loss of $H^{\cdot}$ and N_2. They did not, however, propose a structure for the resultant ion. The presumed intermediate could then eliminate an alkenyl radical to produce the ion of *m/z* 91. In contrast to the spectra of 1-methyl- and 1-ethyl-benzotriazole reported by Maquestiau et al. [4], which have weak ions at *m/z* 104, we found that 1-(secondary-alkyl)benzotriazoles display a very strong peak at *m/z* 104, which was often the base peak for the spectrum. Loss of an alkyl radical fragment from the parent ion of 1-alkylbenzotriazoles can give rise to an iminium cation that can rearrange to either the 1,2,3- or 1,2,4-benzotriazinium ion. This ion readily loses nitrogen to produce the strong peaks corresponding to M minus (N_2R). Elimination of the other alkyl fragment as an alkene produces the ion of *m/z* 104 that is characteristically very strong for the 1-alkylbenzotriazoles. Subsequent loss of HCN from this ion can produce the peak at *m/z* 77.

The mass spectrum of 4-(benzotriazol-2-yl)octane (**2a**) is shown in Figure 3 and is typical for 2-alkylbenzotriazoles. The parent ions of 2-alkylbenzotriazoles are always visible and often stronger than in the 1-isomers. The next most significant ions are due to the combined loss of nitrogen and an alkene fragment, to give ions one mass unit heavier than in the 1-isomer . The loss of nitrogen from the 2-isomer must involve extensive rearrangement, since there is no evidence of initial loss of an alkene fragment, which would give ions at *m/z* 175 and 189. Rearrangement must therefore come first, followed by simultaneous loss of N_2 and alkene, as shown in Figure 4. The base peak of this spectrum at *m/z* 120 corresponds to (BtH_2^+), which presumably arises from elimination of the whole alkyl fragment as an alkenyl radical, after prior hydrogen abstraction (see Figure 4).

Based upon these observations, 1-(**1a–l**) and 2-alkylbenzotriazoles (**2a–l**) can be readily differentiated on the basis of their mass spectra. Maquestiau et al. [4] reported that 1- and 2-ethylbenzotriazole could be differentiated by the fact that the former had a weak ion of *m/z* 104, while the latter had a weak ion of *m/z* 105. We found that 1-alkylbenzotriazoles (**1**) lose an alkyl radical and nitrogen readily to eventually give a very strong peak at *m/z* 104. Although 2-alkylbenzotriazoles (**2**) can lose an alkyl radical and rearrange to the analogous 1,2,4-benzotriazinium ion, they cannot easily lose N_2, since the N = N moiety in this species bears a hydrogen and positive charge. The 1,2,4-benzotriazinium ion intermediate could, perhaps, lose a fragment of RCN to produce an ion of *m/z* 105, but this process is not significant for R groups larger than methyl. Thus, a strong peak at *m/z* 104 is characteristic of 1-alkylbenzotriazoles, while the 2-isomers show very weak ions of *m/z* 104 or 105 (see Figure 5). Because the 1-substituted benzotriazole ring loses nitrogen more

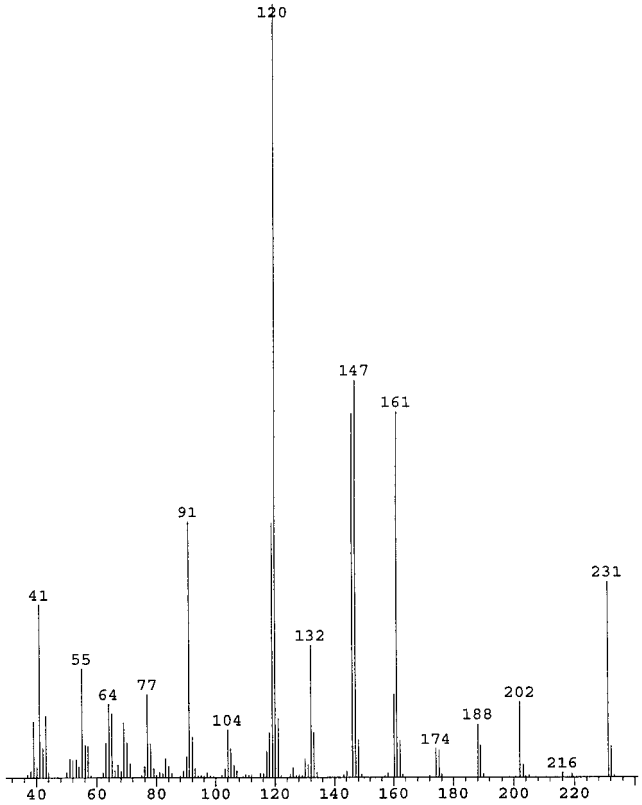


FIGURE 3 EI mass spectrum of 4-(benzotriazol-2-yl)octane.

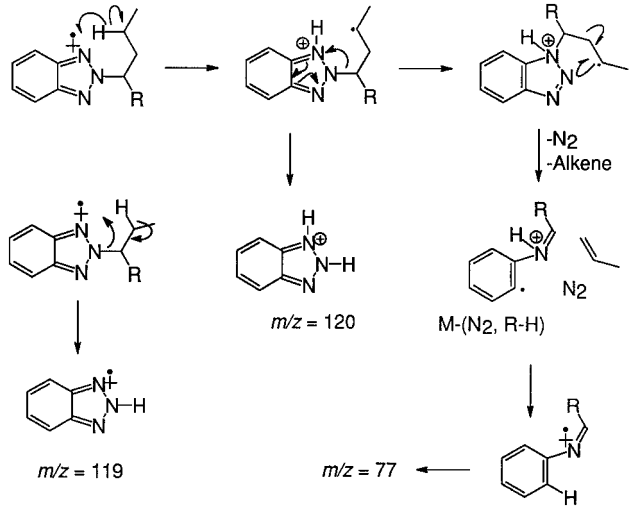


FIGURE 4 General fragmentation scheme for 2-alkylbenzotriazoles.

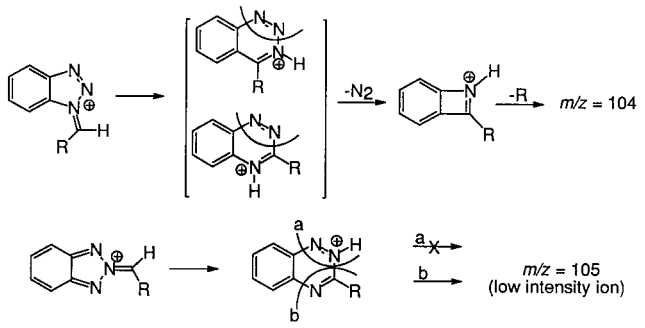


FIGURE 5 Fragmentation to ions of *m/z* = 104 and 105 in 1- and 2-alkylbenzotriazoles.

easily than the 2-substituted analog, peaks due to simple elimination of BtH_n (i.e., $C_6H_nN_3$, centered around *m/z* 119) are small or absent for the 1-isomer, although there is often a cluster of peaks of moderate intensity centered around *m/z* 117 (shown by HRMS to be comprised predominantly (>90%) of fragments with the formula C_8H_nN, where n = 7, 8, 9, and 10). In contrast to this, ions of *m/z* 119 or 120 [shown by HRMS to be mostly (>95%) of formula $C_6H_nN_3$, where n = 5 and 6] are characteristic of 2-alkylbenzotriazoles, which also often constitute the prominent base peak in their spectra. From the HRMS data for 4-(benzotriazol-1-yl)octane (**1a**) shown in Table 1, it can be seen that the major contribution to the *m/z* 119 cluster is from species that have lost nitrogen from the Bt skeleton. On the other hand, the comparable cluster of ions in the HRMS of the isomeric 4-(benzotriazol-2-yl)octane (**2a**) is due very predominantly to species that have retained the three nitrogen atoms from the Bt moiety (see Table 2). However, minor contributions from all combinations are detectable in the HRMS of both isomers.

The location of the benzotriazolyl group along the alkyl chain can also be determined from the mass spectrum, although the location is usually more obvious for the 1-isomer . In 1-alkylbenzotriazoles (**1a–1**), one of the required fragmentations enroute to the strong peak at *m/z* 104 is loss of an alkyl radical α to the point of attachment. In Figure 1, peaks due to M minus propyl and M minus butyl are relatively strong, so the benzotriazole group must be located at C-4. In 2-alkylbenzotriazoles (**2a–1**), the peaks due to loss of [N_2 plus (R minus H)] are relatively weak since simple elimination is the major mode of fragmentation in these molecules. However, peaks due to M-(N_2, propene) and M-(N_2, butene) can be seen in the spectrum of 4-(benzotriazol-2-yl)octane (**2a**) (see Figure 3).

Tables 3, 4, and 5 show the MS data for groups

TABLE 1 HRMS Data for 4-(Benzotriazol-1-yl)octane (**1a**)

Experimental Mass/amu	*Relative Abundance (%)*	*Formula*	*Difference /mmu*	*Theoretical Mass/amu*
117.0611	18	C_8H_7N	−3.2	117.0579
118.0661	41	C_8H_8N	−0.4	118.0657
119.0479	3	$C_6H_5N_3$	0.4	119.0484
119.0737	62	C_8H_9N	−0.2	119.0735
120.0561	6	$C_6H_6N_3$	0.0	120.0561
120.0806	22	$C_8H_{10}N$	0.7	120.0813
121.0854	1.6	$C_7{}^{13}CH_{10}N$	−0.8	121.0846

TABLE 2 HRMS Data for 4-(Benzotriazol-2-yl)octane (**2a**)

Experimental Mass/amu	*Relative Abundance (%)*	*Formula*	*Diffrence /mmu*	*Theoretical Mass/amu*
119.0479	29	$C_6H_5N_3$	−0.2	119.0484
119.0740	6	C_8H_9N	−0.5	119.0735
120.0575	100	$C_6H_6N_3$	−1.3	120.0561
121.0854	1.6	$C_5{}^{13}CH_6N_3$	−0.7	121.0846

of isomeric 1- and 2-alkylbenzotriazoles, where alkyl = pentyl, octyl, and decyl, respectively. In Table 3, the benzotriazol-1-yl isomers (**1**) are distinguished from the benzotriazol-2-yl isomers (**2**) by the presence of strong peaks at *m/z* 104 (entries 1 and 3) and by the fact that the 2-isomers have much stronger peaks at *m/z* 120 (entries 2 and 4). The two N-pentyl isomers with benzotriazole substituted at C-2 (**1b, 2b**) show relatively intense peaks for M minus propyl, while the two isomers with benzotriazole at C-3 (**1c, 2c**) show relatively intense peaks at M minus ethyl, as expected. In a similar fashion, the isomeric octyl- and decyl-benzotriazoles in Tables 4 and 5, respectively, may be distinguished. From the mass spectral data shown in Table 6, the structures of a series of 1-phenylbutylbenzotriazoles can be readily determined. The 1- and 2-isomers are distinguished by the relative intensities of *m/z* 120 and in some cases by the intensities of *m/z* 104. The location of the benzotriazolyl group on the alkyl chain is readily determined in the first two (M minus propyl) and last two entries {M minus [N_2 plus (R minus H)]}. For entries 3 and 4, the expected diagnostic peaks are also present but are very small.

Table 7 shows MS data for miscellaneous pairs of 1- and 2-alkylbenzotriazoles; these isomers can also be readily distinguished using the analysis described above, with particular reference to peaks of *m/z* 117–120.

CONCLUSION

The mass spectra of a wide range of 1- and 2-alkylbenzotriazoles have been examined and found to be

TABLE 3 Mass Spectral Data (*m*/*z*) for a Series of Isomeric (Benzotriazol-1- and -2-yl)pentanes

m/z *M–n*	*189* *0*	*174* *– 15*	*161* *– 28*	*160* *– 29*	*146* *– 43*	*132* *– 57*	*120*	*119*	*118*	*117*	*105*	*104*	*91*
1b 1-(2-Pentyl)benzotriazole (%)	37	2	2	2	34	—	4	23	48	27	11	62	100
2b 2-(2-Pentyl)benzotriazole (%)	33	—	1	2	100	8	30	35	22	10	4	17	38
1c 1-(3-Pentyl)benzotriazole (%)	81	—	8	55	17	—	2	4	13	60	30	100	95
2c 2-(3-Pentyl)benzotriazole (%)	34	1	3	15	1	3	68	100	0	15	3	2	51

TABLE 4 Mass Spectral Data for a Series of Isomeric (Benzotriazol-1-and-2-yl)octanes

m/z *M–n*	*231*	*216* *– 15*	*203* *– 28*	*202* *– 29*	*188* *– 43*	*174* *– 57*	*120*	*11* *9*	*11* *8*	*11* *7*	*10* *5*	*104*	*91*
1d 1-(2-Octyl)benzotriazole (%)	17	17	2	7	44	5	78	56	81	37	10	67	100
2d 2-(2-Octyl)benzotriazole (%)	24	1	1	8	8	5	100	31	12	7	2	6	34
1e 1-(3-Octyl)benzotriazole (%)	21	2	10	59	3	47	18	23	35	43	17	100	56
2e 2-(3-Octyl)benzotriazole (%)	22	3	1	3	1	10	100	0	0	4	3	6	24
1a 1-(4-Octyl)benzotriazole (%)	26	7	2	3	33	27	28	55	49	20	12	100	53
2a 2-(4-Octyl)benzotriazole (%)	28	1	2	11	8	4	100	34	0	3	3	4	29

TABLE 5 Mass Spectral Data for a Series of Isomeric (Benzotriazol-1-and-2-yl)decanes

m/z *M–n*	*259*	*244* *– 15*	*231* *– 28*	*230* *– 29*	*216* *– 43*	*202* *– 57*	*120*	*119*	*118*	*117*	*105*	*104*
1f 1-(2-Decyl)benzotriazole (%)	27	17	1	3	20	9	100	59	71	32	9	59
2f 2-(2-Decyl)benzotriazole (%)	24	1	—	1	7	12	100	22	10	6	2	6
1g 1-(3-Decyl)benzotriazole (%)	19	—	8	47	5	70	32	24	26	43	17	100
2g 2-(3-Decyl)benzotriazole (%)	18	2	1	4	4	4	100	17	3	4	3	7
1h 1-(4-Decyl)benzotriazole (%)	11	—	1	3	50	3	25	58	42	21	12	100
2h 2-(4-Decyl)benzotriazole (%)	14	—	3	15	—	—	100	18	5	2	2	4
1i 1-(5-Decyl)benzotriazole (%)	13	4	2	12	2	36	33	53	45	19	13	100
2i 2-(5-Decyl)benzotriazole (%)	16	1	—	1	4	6	100	17	2	2	1	2

TABLE 6 Mass Spectral Data for a Series of Isomeric (Benzotriazol-1- and -2-yl)-1-phenylbutanes

m/z *M–n*	*251*	*236* *– 15*	*223* *– 28*	*222* *– 29*	*209* *– 43*	*208* *– 44*	*194* *– 57*	*180* *– 71*	*120*	*119*	*118*	*117*	*105*	*104*	*91*
1j 1-(1-Phenylbut-1-yl)Bt (%)	19	—	1	4	8	28	20	100	3	1	3	7	3	12	86
2j 2-(1-Phenylbut-1-yl)Bt (%)	9	1	—	1	3	11	3	23	6	2	4	30	3	9	100
1k 1-(1-Phenylbut-2-yl)Bt (%)	6	—	—	2	—	1	9	2	1	1	7	55	12	35	100
2k 2-(1-Phenylbut-2-yl)Bt (%)	5	1	—	2	—	—	1	2	83	—	9	77	14	14	100
1l 1-(1-Phenylbut-3-yl)Bt (%)	17	—	1	6	7	1	6	10	1	9	19	22	15	20	100
2l 2-(1-Phenylbut-3-yl)Bt (%)	30	1	—	—	—	50	1	10	26	9	36	97	9	23	100

substantially different from those of the simple alkylbenzotriazoles reported in the literature to date. Mass spectral information has been used to distinguish between the 1- and 2-alkylbenzotriazole isomers, as well as to determine the location of the benzotriazolyl moiety on the alkyl chain.

EXPERIMENTAL

All compounds reported in this study were prepared by the acid catalyzed addition of benzotriazole to the appropriate olefin. The complex mixtures of isomeric products were separated by preparative GC and characterized by ^{1}H and ^{13}C NMR, and microanalysis. Full details of the preparation and charac-

TABLE 7 Mass Spectral Data for Pairs of Isomeric (Benzotriazol-1- and -2-yl)alkanes

		m/z for M–n						m/z						
Benzotriazole Substituent		M^+	−15	−28	−29	−43	−57	120	119	118	117	105	104	91
1- and 2-Cyclohexyl	*m/z*	201		173	172	158	144							
1-Cyclohexyl	(%)	100		4	26	40	68	6	30	28	27	8	48	95
2-Cyclohexyl	(%)	45		3	4	2	3	100	31	—	2	3	4	6
1- and 2-Methyl	*m/z*	133												/90
1-Methyl	(%)	100										92	39	65
2-Methyl	(%)	100										5	3	29
1- and 2-Ethyl	*m/z*	147												
1-Ethyl	(%)	41							9	3		5		100
2-Ethyl	(%)	100							16	—		8		95
1- and 2-(2-Propyl)	*m/z*	161	146											
1-(2-Propyl)	(%)	2	42					—	—	4	—	—	5	100
2-(2-Propyl)	(%)	56	13					15	100	—	7	2	1	77
1- and 2-(2,3-Dimethylbut-2-yl)	*m/z*	203	188			160	146							
1-(2,3-Dimethylbut-2-yl)	(%)	13	1			47	—	3	6	21	100	10	3	20
2-(2,3-Dimethylbut-2-yl)	(%)	19	—			100	—	71	54	—	46	6	2	42
1- and 2-(1-Phenylethyl)	*m/z*	223	208	195	194	180	166							
1-(1-Phenylethyl)	(%)	79	9	14	89	88	3	—	1	6	4	100	20	12
2-(1-Phenylethyl)	(%)	49	4	4	29	28	—	1	6	2	1	100	46	12

terization of these compounds are contained in the preceding article [2]. Low-resolution MS data were recorded on a Hewlett-Packard 5972A gas chromatograph/mass spectrometer (Hewlett-Packard Corp., Palo Alto, CA). High-resolution mass measurements were made on a Finnigan MAT 95Q mass spectrometer (Finnigan MAT, San Jose, CA) at an ion source temperature of 200°C.

REFERENCES

[1] A. R. Katritzky, S. Rachwal, G. J. Hitchings, *Tetrahedron, 47,* 1991, 2683; A. R. Katritzky, X. Lan, J. Z. Yang, O. V. Denisko, *Chem. Rev.,* in press.

[2] A. R. Katritzky, I. B. Puschmann, C. V. Stevens, A. P. Wells, *J. Chem. Soc., Perkin Trans., 2,* 1995, 1645.

[3] Q. N. Porter, *Mass Spectrometry of Heterocyclic Compounds,* 2nd ed., Wiley, New York (1985).

[4] A. Maquestiau, Y. Van Haverbeke, R. Flammang, M. C. Pardo, J. Elguero, *Org. Mass Spect., 7,* 1973, 1267.

[5] U. Rapp, H. A. Staab, C. Wunsche, *Org. Mass Spect., 3,* 1970, 45.

[6] R. Lawrence, E. S. Waight, *Org. Mass Spect., 3,* 1970, 367.

[7] J. -L. Aubagnac, R. Jacquier, M.-J. Ramos, *Bull. Chim. Soc. Fr.,* 1974, 3049.

[8] U. Rapp, H. A. Staab, C. Wunsche, *Tetrahedron, 27,* 1971, 2679.