The Elimination of Masses 27 and 28 from the $[M-OH]^+$ Ion of 2-Nitrotoluene

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The expulsion of neutral fragments of masses 27 and 28 from metastable $[M-OH]^+$ ions derived from 2-nitrotoluene has been observed. The relative abundances of the resulting fragment ions, together with the kinetic energy released in each process, has been compared with similar fragmentations of $[C_7H_6NO]^+$ ions derived from other precursor molecules. In this way, the nature of the neutral fragments and the structure of the $[M-OH]^+$ ions from 2-nitrotoluene has been investigated. The most likely structure is the 1,2-benzisoxazolenium cation although the coexistence of other structures cannot be ruled out on the present evidence.

INTRODUCTION

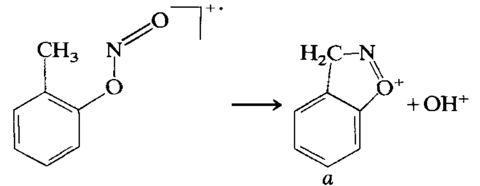
There has been considerable interest in the origin and structure of the m/z 120 ion in the mass spectrum of 2-nitrotoluene (**1**). This ion gives the base peak in the mass spectrum of **1** but is of much lower abundance in the mass spectra of the isomeric 3- and 4-nitrotoluenes.[1] Accurate mass measurement shows its constitution to be $[C_7H_6NO]^+$, proving that it is formed by loss of the elements of hydroxyl from the molecular ion. Furthermore, a metastable peak in the normal mass spectrum, $m^* = 105$, corresponds to the fragmentation:

$$137^+ \rightarrow 120^+ + 17$$

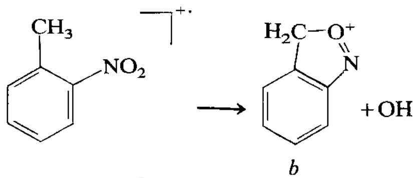
showing that the reaction can occur from metastable molecular ions.[1]

The oxygen atom in the expelled $OH^\cdot$ must originate from the nitrogroup, but there is a choice of origins for the hydrogen atom. Meyerson and coworkers[2] examined the behaviour of α-d-2-nitrotoluene, concluding that since an easily detectable isotope effect was observed, then the methyl group is the major source of the hydrogen atom. Butcher and Thomas[3] have pointed out that the observation of a large kinetic isotope effect is not conclusive proof of such a process. They synthesized α,α,α-d_3-2-nitrotoluene and recorded its mass spectrum. From this they concluded that the loss of $OH^\cdot$ does exclusively involve the hydrogen atoms on the methyl group.

A number of mechanisms have been put forward for the expulsion of $OH^\cdot$ from 2-nitrotoluene molecular ions. Beynon and coworkers[1,4] have suggested two possibilities. In the first, the molecular ion undergoes rearrangement to the nitrite form before fragmentation (Scheme 1). Such a rearrangement of the molecular ion has been suggeted to occur[5] during the expulsion of $NO^\cdot$ (a fragmentation characteristic of aromatic nitro compounds). In the second mechanism, no rearrangement of the molecular ion is invoked (Scheme 2). Both of the resulting m/z 120 ions a and b are bicyclic, the difference being the location of the oxygen and nitrogen atoms.

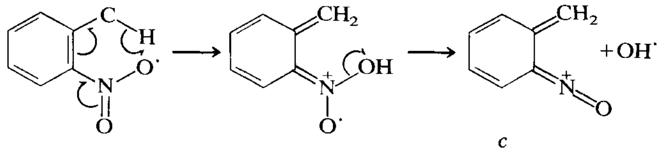


Scheme 1



Scheme 2

Meyerson and coworkers[2] have suggested that the fragmentation may occur via an intermediate and that the resultant m/z 120 ion (c) might not contain a second ring (Scheme 3).



Scheme 3

Further fragmentation of the m/z 120 ion is demonstrated by the occurrence of a metastable peak at $m^* = 70.5$ in the normal mass spectrum.[4] This corresponds to expulsion of mass 28 from the ion of mass 120. Of the possible identities for this mass 28 neutral fragment ($CO, H_2CN^\cdot$ and C_2H_4), the most likely is CO. The fact that the m/z 92 peak in the mass spectrum consists mainly of $[C_6H_6N]^+$ ions supports this contention. The carbon atom of the CO could originate from the methyl group (for instance in b) or from the phenyl ring (as might be expected in a). In order to investigate this, Beynon and coworkers[4] examined

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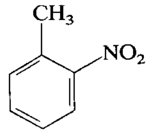
the high resolution mass spectrum of α-^{13}C-2-nitrotoluene in the region of m/z 92 and 93. It was observed that the ^{13}C atom is lost when the $[M-OH]^+$ ion loses CO within the ion source. The conclusion that *b* is the structure of the $[M-OH]^+$ ion was thus drawn, so that the mechanism given in Scheme 2 would seem to better account for the fragmentation sequence.

In order to investigate this problem further, we have undertaken a study of $[C_7H_6NO]^+$ ions by mass analysed ion kinetic energy (MIKE) spectrometry.

The metastable m/z 120 fragment ions generated by electron impact ionization from 2-nitrotoluene (**1**), 2-nitrosotoluene (**2**), anthranilic acid (**3**), 1-*tert*-butyl-2,1-benzisoxazoline (**4**) and 2-*tert*-butyl-1,2-benzisoxazoline (**5**) were examined. Similarly, the metastable $[M+1]^+$ ions generated by methane chemical ionization (CI) of 1,2-benzisoxazole (**6**), 2,1-benzisoxazole (**7**) and 2-cyanophenol (**8**) were studied. With a view to identifying the mass 28 neutral fragments expelled unimolecularly from most of these ions, deuterium labelling experiments were also undertaken. Fragmentation with loss of a neutral fragment of mass 27 is a feature of the spectra and this fragmentation process has also been investigated. In the cases of compounds **4** and **5**, a single deuterium atom was substituted in the 3-position. For anthranilic acid (**3**), all three labile hydrogen atoms were substituted by exchange with D_2O. Labelling of the ions generated by CI from **6** and **7** was achieved by the use of methane-d_4 as reagent gas.



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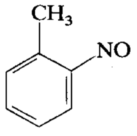

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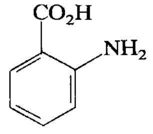

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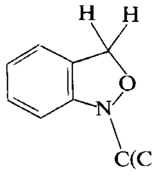

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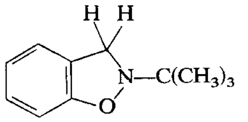

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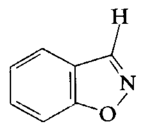

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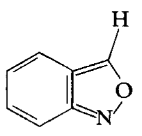

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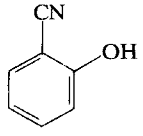

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RESULTS AND DISCUSSION

2-Nitrotoluene (1)

The MIKE spectrum of $[C_7H_6NO]^+$ ions derived from 2-nitrotoluene (**1**) shows major peaks due to the loss of mass 27 and 28 (Fig. 1). These peaks are broadened by kinetic energy release such that they are not well resolved. After geometrical deconvolution (assuming that the 92^+ peak is symmetrical), it is seen, from Fig. 1, that while the peak for the process $120^+ \rightarrow 93^+ + 27$ is gaussian in shape, that for $120^+ \rightarrow 92^+ + 28$ is more complex. The peak heights are in approximately a 3:2 ratio. From the peak shapes, it is conjectured that the expulsion of mass 27 is probably a single process, but there may be two processes involving the loss of mass 28. This latter situation could arise by the existence of more than one structure for the parent $[C_7H_6NO]^+$ ions, by there being more than one identity for the expelled mass 28 neutral or by the formation of two isomeric products. The MIKE spectra of the remaining samples were then compared with this spectrum. Identity of spectra, both with regard to relative abundances and peak widths would indicate identical structures for the m/z 120 ions.

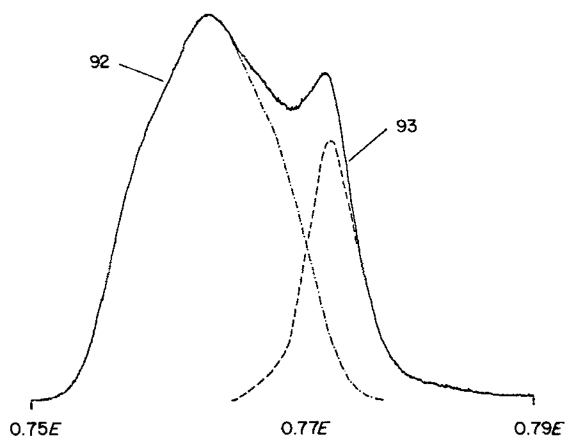

Figure 1. Partial MIKE spectrum of $[C_7H_6NO]^+$ ions from **1**.

2-Nitrosotoluene (2)

The expulsion of H˙ from the molecular ions of 2-nitrosotoluene gives $[C_7H_6NO]^+$ ions. The most probable source of the hydrogen radical is the methyl group and hence the structure of the m/z 120 ions is likely to be *c* or possibly *b*. The MIKE spectrum shows that loss of mass 28 is approximately five times as probable as loss of mass 27 (Fig. 2(a)). The kinetic energy releases during the fragmentation processes are also very different from those for the peaks in Fig. 1.

Anthranilic acid (3)

Anthranilic acid is isomeric with 2-nitrotoluene and, hence, the expulsion of OH˙ from the molecular ion gives $[C_7H_6NO]^+$ ions. In common with simple aromatic carboxylic acids, it is envisaged that the OH˙ is eliminated largely from the acid function.[6] It is assumed that the resultant ions do not cyclize, although there is no direct evidence for this. The loss of mass 28 from these ions is seen from the MIKE spectrum to be about twice as possible as that of 27 (Fig. 2(b)). This observation is in keeping with the known behaviour of aromatic carboxylic acids in consecutive loss of OH˙ and CO.[7] The identity of the mass 28 neutral fragment is confirmed to be CO by deuterium labelling. A

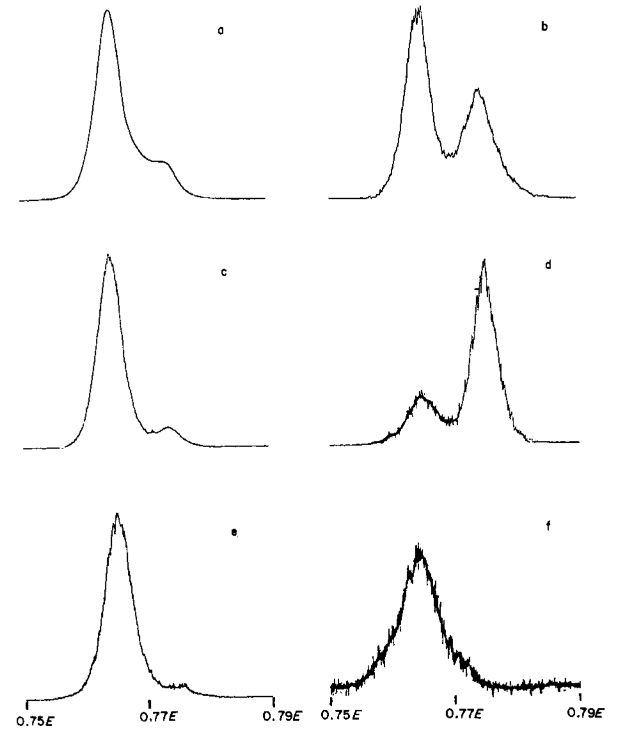

Figure 2. Partial MIKE spectrum of $[C_7H_6NO]^+$ ions from (a) **2**, (b) **3**, (c) **4**, (d) **6**, (e) **7**, (f) **8**.

sample of anthranilic acid was partly deuterated by exchange. The mass spectrum of the resulting solid showed molecular ions with partial and complete deuteration of the three labile hydrogen sites. The $[C_7H_4D_2NO]^+$ ions (m/z 122) can arise by loss of $OD^{\cdot}$ from the d_3 molecular ions or of $OH^{\cdot}$ from d_2 molecular ions. The net result is the same. The MIKE spectrum of these ions showed loss of mass 28 but not of mass 27. This suggests that loss of HCN from $[C_7H_6NO]^+$ ions of anthranilic acid becomes loss of DCN from $[C_7H_4D_2NO]^+$ ions from the deuterated compound. The loss of CO from both compounds remains. Once again, the kinetic energy release during loss of CO is less than for the fragmentation reaction in 2-nitrotoluene, indicating different structures for the m/z 120 ions in the two cases.

1-*tert*-Butyl-2,1-benzisoxazoline (4)

Cleavage of the exocyclic carbon–nitrogen bond in the molecular ions of **4** would result in expulsion of $\dot{C}(CH_3)_3$ and the generation of $[C_7H_6NO]^+$ ions. These ions would presumably be bicyclic in structure. The MIKE spectrum of these ions shows that the loss of mass 28 is more probable than that of 27 by a factor of nearly 10:1 in this case (Fig. 2(c)). The MIKE spectrum of the $[M-C(CH_3)_3]^+$ ions from the 3-d_1 analogue was also obtained. The results were consistent with the hydrogen atom at the 3-position being involved in the loss of mass 27 (HCN) but not in loss of 28 (CO), the peak for the loss of mass 27 being reduced in height by approximately 50% relative to that for loss of 28 in the deuterated compound. The structure of the m/z 120 ion is, again, obviously different from that in 2-nitrotoluene.

2-*tert*-Butyl-1,2-benzisoxazoline (5)

Following a similar argument to that given above for **4**, expulsion of $\dot{C}(CH_3)_3$ from the molecular ions of **5** gives $[C_7H_6NO]^+$ ions having a cyclic structure. The MIKE spectrum shows a 5:2 abundance ratio in favour of the loss of mass 28 over 27 (Fig. 3(a)). The peak due to loss of mass 28 is complex and similar in shape to the corresponding peak for 2-nitrotoluene (**1**). Geometrical deconvolution of these peaks, in a similar manner to that in Fig. 1, shows how the overall peak shape could arise. The close similarity between these peaks and the corresponding peaks for **1** is illustrated in Fig. 4 where the two spectra are superimposed. Deuterium labelling at the 3-position changes this region of the MIKE spectrum markedly (Fig. 3(b)). The loss of mass 27 is greatly reduced relative to that of 28 (6:1 ratio of m/z 93:m/z 94) and the peak

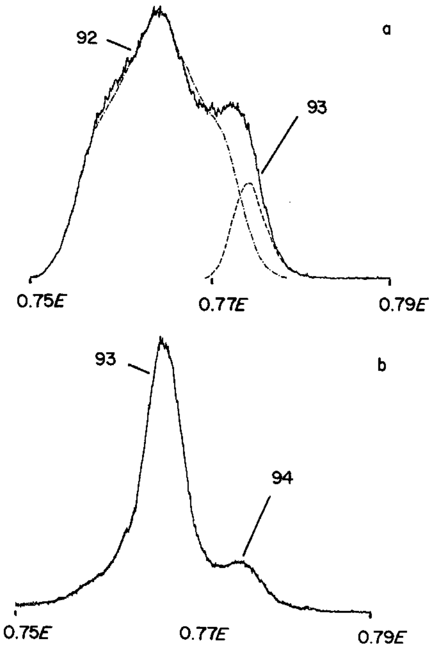

Figure 3. Partial MIKE spectrum of (a) $[C_7H_6NO]^+$ ions from **5**, (b) $[C_7H_5DNO]^+$ ions from 3d_1-2-*tert*-butylbenzisoxazoline.

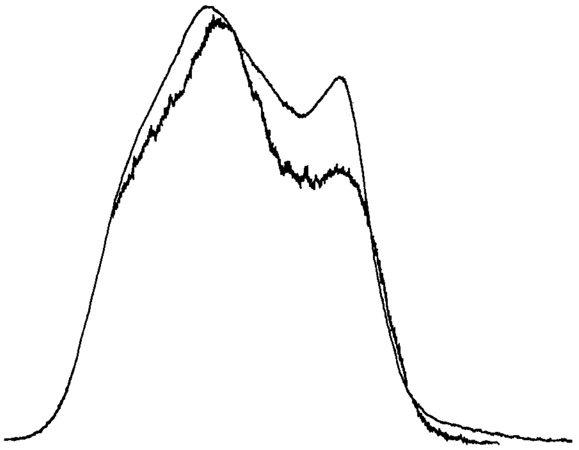

Figure 4. Comparison of the MIKE peaks for the processes $120^+ \rightarrow 93^+ + 27$ and $120^+ \rightarrow 92^+ + 28$ from $[C_6H_7NO]^+$ ions of **1** and **5**.

for the loss of mass 28 is much narrower than that in the undeuterated compound. The narrowness of this peak can be explained by the major contribution to it being due to DCN loss rather than CO loss. The relatively minor loss of unlabelled HCN shows that it is mainly the 3-position on the ring that is involved in this fragmentation process.

1,2-Benzisoxazole (6)

Generation of the $[M-H]^+$ ion of **6** under methane CI conditions gives $[C_7H_6NO]^+$ ions. Protonation of the neutral molecule on either nitrogen or oxygen would give stable species, with the first of these perhaps being the more stable. The MIKE spectrum shows that loss of mass 27 is favoured over that of 28, this being the only compound in the present study which behaves in this way (Fig. 2(d)). The use of methane-d_4 as CI reagent gas confirmed that the mass 28 neutral is CO rather than $H_2CN^{\cdot}$ or C_2H_4.

2,1-Benzisoxazole (7)

This compound is isomeric with **6** and methane CI generates $[M+H]^+$ ions in a similar manner. Protonation at either oxygen or nitrogen is again possible. Preferential elimination of mass 28 from these ions is shown in the MIKE spectrum (Fig. 2(e)). The loss of mass 27 is almost absent in this case. Again, the use of methane-d_4 as CI reagent gas confirms that the eliminated mass 28 neutral is CO rather than $H_2CN^{\cdot}$ or C_2H_4.

2-Cyanophenol (8)

Protonation of this compound under CI conditions is assumed to give rise to $[C_7H_6NO]^+$ ions possessing a monocyclic structure. Attachment of H^+ onto either nitrogen or oxygen is possible, although the latter would probably give the more stable product. Expulsion of mass 27 and 28 from these ions proved to have a low probability, and only a weak peak for the loss of 28 was observed (Fig. 2(f)). The use of methane-d_4 as CI reagent gas did not displace this peak, indicating that it is probably due to the loss of CO.

Kinetic energy release

The measurement of kinetic energy release (KER) during fragmentation of metastable ions is a technique which is frequently used as a probe of ion structure.[7,8] The relative product ion yields from competing fragmentations of metastable ions are more dependent upon the internal energy distribution of the precursor ions than is the kinetic energy release. The results given above have been mainly concerned with the relative abundances of m/z 92 and m/z 93 and the evidence concerning ion structure based on kinetic energy release will now be considered. Due to difficulties of overlapping of peaks and weak signals in some instances, it has not been thought worthwhile to attempt to list measured KER values but instead to compare in a qualitative manner the peak shapes obtained from the various compounds. It can be seen by inspection of Fig. 2 that the kinetic energy released upon loss of neutral CO (left-hand peak in each case) is very similar in compounds **2**, **3**, **4**, **6** and **7**. The similarity in the case of compounds **2**, **3**, **4** and **7** is reasonably rationalized in terms of a common ion structure, though this is difficult to visualize in the case of compound **6**. The energy released in the expulsion of mass 27 from these ions is less diagnostic of structure. There are some similarities in the case of **1**, **5** and **7** and also between **2**, **4** and **6**. The $[C_7H_6NO]^+$ ions from **2** and **4** can be envisaged as sharing a common structure, but it is difficult to see how **6** could give ions of similar structure. The lack of similarity in the data for **4** and **7** and for **5** and **6** seems worthy of note and may indicate that the site of proton attachment in the chemical ionization experiments is of importance.

Closely similar ion kinetic energy peaks for loss of both mass 28 and mass 27 for compounds **1** and **5** suggest that these reacting ions share a common structure. The range of kinetic energy releases for loss of mass 28 from all structures is wide, underlining the importance of this fragmentation pathway as a structural probe. It is only ions from **5** that give an energy release as large as that from 2-nitrotoluene and **5** is also the only compound that gives a composite peak similar in shape to that from 2-nitrotoluene. When the ion kinetic energy peaks from the two compounds are overlaid (see Fig. 4) it can be seen that there is an excellent match as far as kinetic energy release is concerned, though a significant difference in the relative abundances of the two peaks from the two compounds. This suggests that the fragmenting structure is, in fact, the same in both cases, the difference in relative abundances indicating a difference in the internal energy distributions. On this evidence, the formation of $[C_7H_6NO]^+$ ions having a 1,2-benzisoxazolenium cation (a) structure when $OH^{\cdot}$ is expelled from molecular ions of 2-nitrotoluene is suggested. It is interesting to note that if this conclusion is correct, then the carbon atom involved in the loss of CO originates from the phenyl ring. Previous work concluded that when CO was expelled from $[M-OH]^+$ ions of 2-nitrotoluene in the ion source, the carbon atom involved originated from the methyl group.[4] In the rapid series of fragmentations occurring in the ion source, rearrangement, which is intrinsically slow, would be less likely. For metastable ion fragmentations, however, more time is allowed for the slower rearrangement processes to occur. The expulsion of CO from ions such as b^4 is, thus, suggested to be more likely for fast reactions. Thus, structure b may be generated from 2-nitrotoluene *molecular ions* within the ion source and if rearrangement allows loss of CO from ions of lower internal energy than can fragment from c, it is b that will fragment in the metastable time-frame.

EXPERIMENTAL

Mass spectrometry

All MIKE spectra were obtained using a VG Analytical ZAB-2F mass spectrometer equipped with a combined EI/CI source[9] and an associated data system.[10] Samples were introduced into the ion source using the direct insertion probe, septum and all-glass heated inlet systems. Standard electron impact source conditions were 70 eV electron impact energy, 100 μA trap current and 160 °C source temperature. The pressure indicated near the throat of the source diffusion pump was maintained at a constant value for each sample, the measured pressure being between 4×10^{-8} Torr and 2×10^{-6} Torr, depending on the sample and inlet system used. Standard chemical ionization conditions involved introduction of sample until the source ion gauge gave an indication of $5\text{–}8\times10^{-7}$ Torr (from a background pressure of 5×10^{-8} Torr), followed by introduction of reagent gas to give a reading of 2×10^{-5} Torr.

The background pressure in the second field free region was 3×10^{-8} Torr and a minimum energy resolution (at half peak height) of 700 ppm for CI experiments and 500 ppm for EI experiments was used.

Materials

2-Nitrotoluene, 2-nitrosotoluene, anthranilic acid and 2-cyanophenol were all obtained commercially.

2,1-Benzisoxazole (**7**) was prepared by reducing 2-nitrobenzaldehyde with tin and glacial acetic acid using the method of Friedländer and Henriques[11]; this gave **7** (68%), b.p. 102–103 °C (15 mm) (Ref. 11 gives b.p. 99–99.5°C (13 mm)).

1,2-Benzisoxazole (**6**) was prepared by the method of Kemp and Woodward;[12] this gave **6** (90%), b.p. 34 °C (2 mm) (Ref. 12 gives b.p. 35–38 °C (2 mm)).

The *tert*-butyl-substituted benzisoxazolines **4** and **5** were prepared from the corresponding benzisoxazoles **7** and **6** via their *N*-*tert*-butyl perchlorate salts.[13]

1-*tert*-Butyl-2,1-benzisoxazolium perchlorate was prepared from **7** by the method of Coombs and Hardtmann[13] as an orange solid (88%), m.p. 137–138 °C dec. (Ref. 13 gives m.p. for BF_4^- salt 132–134 °C dec.).

Similarly prepared from **6** was 2-*tert*-butyl-1,2-benzisoxazolium perchlorate as a pale pink solid (83%), m.p. 165–166 °C (softens at 161 °C).

1-*tert*-Butyl-2,1-benzisoxazoline (**4**) was prepared by sodium borohydride reduction[13] of the perchlorate salt prepared from **7**; this gave **4** (44%), b.p. 62–72 °C (0.3 mm) (Ref. 13 gives b.p. 90–100 °C (0.2 mm)).

Similar reduction of the perchlorate salt prepared from **6** gave 2-*tert*-butyl-2,1-benzisoxazoline (**5**) (10%), m.p. 143–144 °C. Infrared (KBr disc): 3450, 3190, 3110, 2990, 2220, 1600, 1470, 1440, 1270, 1250, 1115, 1065, 1040 cm^{-1}. ^{1}H NMR, δ($CDCl_3$): 1.23 (s, 9H), 3.96 (s, 2H), 6.6–7.5 (m, 4H).

Reduction of the perchlorate salts with sodium borodeuteride gave the 3-d_1 analogues of **4** and **5**.

Deuterium labelling of **3** was achieved by shaking with D_2O and a little hydrochloric acid catalyst in ethanol solution. The solvent was evaporated off under reduced pressure.

Acknowledgements

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REFERENCES

1. J. H. Beynon, R. A. Saunders and A. E. Williams, *Ind. Chim. Belg.* **29**, 311 (1964).
2. S. Meyerson, I. Puskas and E. K. Fields, *J. Am. Chem. Soc.* **88**, 4974 (1966).
3. A. R. Butcher and C. B. Thomas, *Org. Mass Spectrom.* **14**, 448 (1979).
4. J. H. Beynon, R. A. Saunders, A. Topham and A. E. Williams, *J. Chem. Soc.* 6403 (1965).
5. J. H. Beynon, M. Bertrand and R. G. Cooks, *J. Am. Chem. Soc.* **95**, 1739 (1973).
6. H. Budzikiewicz, C. Djerassi and D. H. Williams, *Mass Spectrometry of Organic Compounds*, p. 219, Holden-Day, San Francisco (1967).
7. K. Levsen, *Fundamental Aspects of Organic Mass Spectrometry*, p. 238, Verlag Chemie, Weinheim (1978).
8. R. G. Cooks, J. H. Beynon, R. M. Caprioli and G. R. Lester, *Metastable Ions*, p. 118, Elsevier, Amsterdam (1973).
9. R. P. Morgan, J. H. Beynon, R. H. Bateman and B. N. Green, *Int. J. Mass Spectrom. Ion Phys.* **28**, 171 (1978).
10. P. D. Bolton, G. W. Trott, R. P. Morgan, A. G. Brenton and J. H. Beynon, *Int. J. Mass Spectrom. Ion Phys.* **29**, 179 (1979).
11. P. Friedländer and R. Henriques, *Ber. Deut. Chem. Ges.* **15**, 2105 (1882).
12. D. S. Kemp and R. B. Woodward, *Tetrahedron* **21**, 3019 (1965).
13. R. V. Coombs and G. E. Hardtmann, *J. Org. Chem.* **35**, 2440 (1970).

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