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ELECTRON IMPACT STUDIES—XLIX[1]

THE $C_{13}H_9$ SKELETAL-REARRANGEMENT FRAGMENT IN THE MASS SPECTRA OF BENZYL PHENYL KETONE DERIVATIVES

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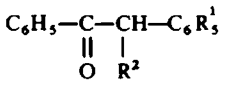
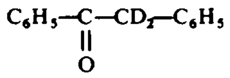
Abstract—The spectra of benzyl phenyl ketone derivatives contain ions at *m/e* 165 ($C_{13}H_9$) which are produced by skeletal-rearrangement processes. The rearrangement peak is most pronounced in the spectrum of the oxime of benzyl phenyl ketone where it arises mainly from an M—H_2O species. Deuterium labelling studies and metastable characteristics are consistent with the M − 18 species having the properties of a 2,3-diphenyl-2-H-azirine molecular ion.

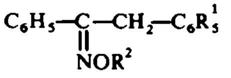
THE formation of *m/e* 165 ($C_{13}H_9$) by skeletal-rearrangement processes has been observed in the mass spectra of stilbene and related compounds,[2-6] 9,10-dihydrophenanthrene,[4-6] and a variety of diphenyl heterocyclic systems.[4,7-12] As a continuation of this work, we have examined the spectra of the benzyl phenyl ketone derivatives (**1**–**11**) in order to see whether ions at *m/e* 165 (best represented as the fluorene cation) occur, and to study the modes of formation of any such rearrangement species.

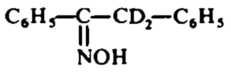

$C_6H_5{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{R^2}{|}}{CH}{-}C_6R^1_5$


$C_6H_5{-}\underset{\underset{O}{\|}}{C}{-}CD_2{-}C_6H_5$

4

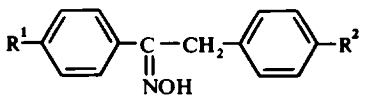
1: $R^1 = H$, $R^2 = H$
2: $R^1 = D$, $R^2 = H$
3: $R^1 = H$, $R^2 = CHO$


$C_6H_5{-}\underset{\underset{NOR^2}{\|}}{C}{-}CH_2{-}C_6R^1_5$


$C_6H_5{-}\underset{\underset{NOH}{\|}}{C}{-}CD_2{-}C_6H_5$

8

5: $R^1 = H$, $R^2 = H$
6: $R^1 = H$, $R^2 = D$
7: $R^1 = D$, $R^2 = H$



9: $R^1 = MeO$, $R^2 = H$
10: $R^1 = H$, $R^2 = MeO$
11: $R^1 = Me_2N$, $R^2 = Me_2N$

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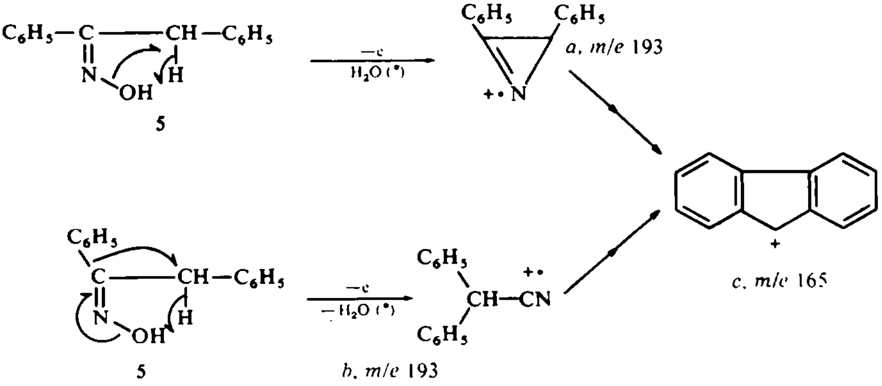
TABLE 1. FORMATION OF *m/e* 165 IN THE SPECTRA OF **1**, **3**, **5** AND **9–10**
(All processes are substantiated by metastable peaks)

Compound	Processes producing *m/e* 165	Abundance of *m/e* 165 (%)
1	$M—H^{\bullet}—CO—H_2$	2
3	$M—CO—H^{\bullet}—CO—H_2$	8
5	$M—H_2O—HCN—H^{\bullet}$ (see below)	20
9	$M—H_2O—CH_2O—HCN—H^{\bullet}$	8
10	$M—H_2O—CH_2O—HCN—H^{\bullet}$	4

All the spectra except that of **11**, contain an ion at *m/e* 165. The abundances of this ion and the processes producing it are recorded in Table 1. The all-over process for the formation of *m/e* 165 in the spectrum of benzyl phenyl ketone (**1**) is $M—CH_3O$. The three H atoms involved in this rearrangement come almost randomly from the whole molecule as evidenced by the spectra of **2** and **4**. For example the peak at *m/e* 165 in the spectrum of **1** is shifted to 165, 166 and 167 in that of **4**. The observed ratio of the abundances of 165/166/167 is 2:10:12, in reasonable agreement with the theoretical ratio (for random loss of three H atoms) 1:9:12.

The rearrangement is most pronounced (Table 1) in the spectrum (Fig. 1) of the oxime (**5**), and decreases predictably as substituents are placed on the aromatic rings (e.g. **9–11**, Table 1). The genesis of *m/e* 165 in the spectrum of **5** has been studied by deuterium labelling and by the application of metastable characteristics.[13-19]

There are three processes which give rise to *m/e* 165 in the spectrum of **5**; viz. (i) $M—H_2O—HCN—H^{\bullet}$; (ii) $M—H_2O—H_2CN$, and (iii) $M—HO^{\bullet}—HCN—H_2$. All eliminations are substantiated by metastable peaks (represented by an asterisk in a Fig. or in the text). The 70 eV spectra of the labelled compounds **6**, **7** (Fig. 1) and **8** show the loss of water from the molecular ion to be hydrogen-specific, involving the OH group and a benzylic hydrogen. This is of particular interest and indicates that hydrogen randomization does not precede this elimination, although the spectra of and **8** show that the production of the d_2- and d_5-tropylium cations (*m/e* 93 and 96 respectively) does proceed with hydrogen scrambling of the phenyl and benzylic hydrogens and/or deuteriums, (cf. fragmentation of the labelled ethylbenzenes[20]). Two possible structures may now be written to account for the formation of *m/e* 165 (*c*) from the $M—H_2O$ species, i.e. **5**→*a*→*c* and **5**→*b*→*c*.



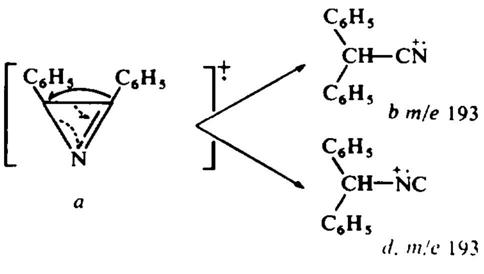
The partial spectra of 2,3-diphenyl-2-H-azirine[21] (**12**) and diphenylacetonitrile (**13**) are recorded in Fig. 2. Both spectra contain pronounced peaks at *m/e* 165, and to determine whether *a* or *b* corresponds to the M—H_2O species in the spectrum of **5**, the ratios of the abundances of the metastable peaks for the 193 → 166 transitions, to the abundances of *m/e* 166 have been compared at various energies of the electron beam for all spectra (Table 2). In addition, metastable profiles are illustrated in Figs. 3 and 4. The metastable peak shapes in the *m/e* 140–144 regions in the spectra of the oxime **5** and the nitrile (**13**) are quite different, as are the ratios of *m/e* 166/m* in both spectra. The M-18 species therefore does not correspond to *b*.

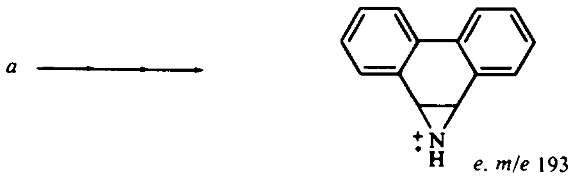
Table 2†. Ratios of the relative abundances of *m/e* 166 to the metastable peak at *m/e* 142·8 (193→166) in the spectra of **5** and **12**–**14**

Compound	70 eV	40 eV	30 eV	20 eV	15 eV
Oxime (**5**)	31	29	27	23	17
Azirine (**12**)	40	39	37	32	24
Nitrile (**13**)	74	72	70	64	49
Isonitrile (**14**)	140	132	118	97	73

† The *m/e* 165 isotope peak has been substracted to give the correct abundance of *m/e* 166. Experimental error in the *m/e* 166/m* ratio is ±5%, calculated from an average of ten measurements.

The corresponding metastable shapes in the spectra of **5** and **12** are similar, except that three metastable peaks are observed for **5** and only two for the azirine (**12**). The additional metastable peak (*m/e* 143·8) in the spectrum of **5** is that for the *m/e* 194 (M—HO·) → 167 elimination, a process which cannot occur for **12**. The *m/e* 166/m* ratios do not agree within experimental error, but the discrepancy is small enough to be accounted for by the presence of the third metastable ion (in the spectrum of **5**) which would have the effect of slightly increasing the abundance of the metastable peak at *m/e* 142·8 (m*). It appears reasonable to propose that those portions of the M-18 species (of **5**) and of the 2,3-diphenyl-2-H-azirine molecular ion which give rise to *m/e* 166 and 165, have the same structure. Although *a* is probably produced initially in both cases, it is unlikely to be the species which eliminates HCN, and we will provide evidence (below) to show that *m/e* 166 and 165 are produced from a rearranged 2,3-diphenyl-2-H-azirine molecular ion, possibly *e* or a tautomeric structure.





e. *m*/*e* 193

There are two general mechanisms for loss of HCN from *a*. One involves a cyclization of the type proposed to explain the formation of *c* from 4,5-diphenylimidazole,[5] or perhaps stilbene.[2,6] The other involves specific phenyl migration. Phenyl migration may produce either the nitrile (*b*) or isonitrile (*d*) radical ions. Comparison of the metastable characteristics (above) preclude the intermediacy of the diphenylacetonitrile radical ion (*b*), and a similar comparison with the corresponding isonitrile (Table 2 and Fig. 4) shows that it is not involved in the rearrangement. A cyclization mechanism is therefore favoured, but ^{13}C labelling would be necessary to prove that a cyclic intermediate (e.g. *e*, or a tautomeric structure) accounts for the formation of the fluorene cation.

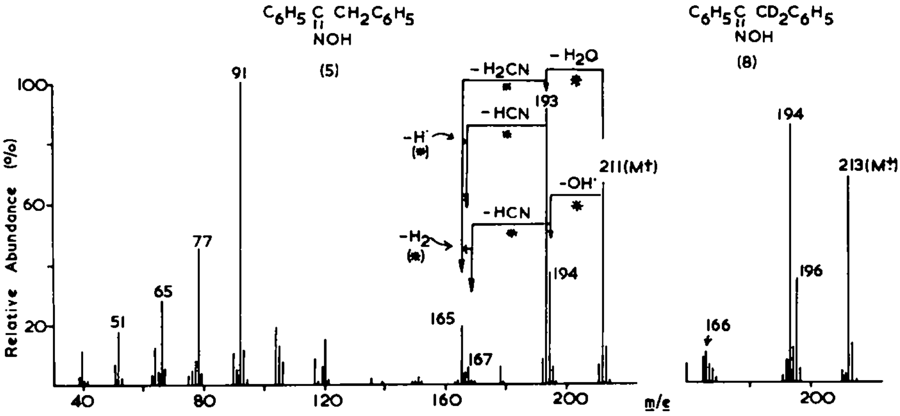


FIG. 1

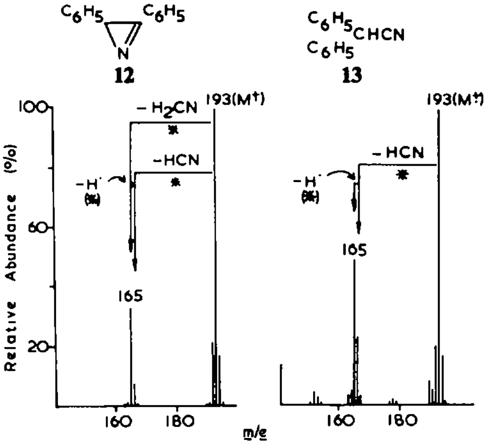


FIG. 2

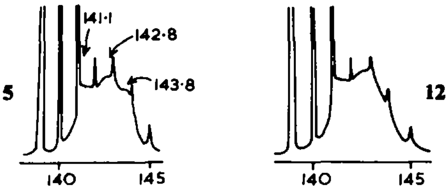


FIG. 3

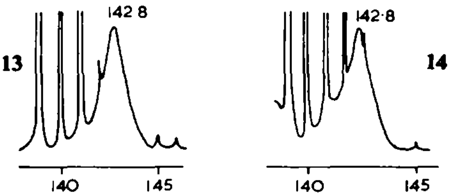


FIG. 4

EXPERIMENTAL

Mass spectra were determined with an Hitachi Perkin–Elmer RMU 6D double-focusing mass spectrometer operating at 70 eV (unless otherwise specified). Samples were introduced through an all glass heated inlet system at approximately 100°.

All unlabelled compounds were prepared by known procedures. Compound 2 was prepared by the reaction of $d_7$benzylmagnesium bromide with benzaldehyde, followed by Jones oxidation to the d_7-ketone. The d_7-ketone was heated under reflux in water containing sodium carbonate for 24 hr producing 2 (>95% d_5).

Compound 4 was prepared by heating benzyl phenyl ketone under reflux in D_2O containing Na_2CO_3 (isotopic purity of 4 > 95% d_2).

Compound 6 was prepared by stirring a benzene solution of 1 with D_2O for 24 hr (isotopic purity of 6, $d_0 = 12$, $d_1 = 88\%$). Introduction of 5 directly into the source with D_2O[22] produced a d_1-derivative.

Compounds 7 and 8 were prepared by treating 2 and 4 respectively with hydroxylamine hydrochloride.

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