

JMS Letters

Dear Sir,

Comment on the Reported *tert*-Butyl Group Migration in the Mass Spectrum of Phenyl Pivalate†

Extensive reports are available in the literature regarding skeletal rearrangements involving the migration of atoms and groups accompanied by the loss of neutral molecules such as H₂O, CO, CO₂ and NH₃ under electron impact ionization.^{1–3} One such report is the migration of the *tert*-butyl group to the aromatic ring accompanied by the loss of CO₂ in the mass spectrum of phenyl pivalate,⁴ and this report is often cited as a reference for alkyl group migration under electron impact ionization.^{5–8} Based on this report, the loss of 43 u from the molecular ion in the mass spectrum of *N*-phenylpivalamide was attributed to the loss of the NHCO moiety and the migration of *tert*-butyl group to the aromatic ring by another group.⁹

During the course of synthesizing some model compounds for mass spectral studies, we prepared phenyl pivalate and characterized it by its mass spectrum. To our surprise, we found an ion at *m/z* 135 corresponding to the loss of 43 u from the molecular ion and not *m/z* 134 as reported earlier. We confirmed the results with three different mass spectrometers. Intrigued by this observation, we undertook a detailed mass spectral study of phenyl pivalate (1), *S*-phenyl thiopivalate (2) and *N*-phenylpivalamide (3).

Compounds 1–4 were prepared by reported methods and characterized by their NMR and IR spectra. The mass spectra were measured in a VG Autospec-M mass spectrometer operated at a source temperature of 200 °C and an electron energy of 70 eV with a trap current of 200 μA. All the samples were introduced through an HP 5890 gas chromatograph equipped with an OV-1 fused silica capillary column. High-resolution spectra were measured at 8000 resolution for 1, 2 and 4 and 15000 resolution for 3. All the collision-induced dissociation (CID) spectra were recorded using the linked-scan technique at constant *B/E* and helium was used as the collision gas.

The mass spectra of 1, 2 and 3 are given in Table 1. The fact that no ion corresponding to the loss of COS is observed in the mass spectrum of 2 confirms our finding that the mass assignment in the reported mass spectrum of 1 is wrong. All three compounds uniformly give ions corresponding to the loss of 43 u from the molecular ion. The formation of the [M – 43]⁺ ion in 1 and 2 can be explained by the loss of C₃H₇[•] and/or C₂H₃O[•] from M⁺. Accurate mass measurement at 8000 resolution shows that the loss of C₂H₃O[•] occurs exclusively in 1 and 2 and the [M – 43]⁺ ion corresponds to C₉H₁₁O (135.0813) and C₉H₁₁S (151.0580) in 1 and 2 respectively. An additional possibility, namely the loss of the NHCO group, also exists in 3. The resolution needed to differentiate the loss of C₂H₃O[•] from NHCO is around 11 000. Accurate mass measurement at 15 000 for 3 (134.0969) established again that the loss of 43 u in 3 corresponds to C₂H₃O[•] and not to NHCO as reported earlier. Hence the present findings not only corrects the mistakes reported in the literature but also shows that there is no migration of the *tert*-butyl group as envisaged earlier.

The parent ion scan of *m/z* 135 in 1 gives [M – CH₃]⁺ as a major precursor and [M – CO]⁺ and M⁺, as the minor precursors. For 2 and 3, M⁺ was identified as the major precursor and [M – CH₃]⁺ and [M – CO]⁺ as minor precursors.

† ICT Communication No. 3678.

Table 1. Electron impact spectra of compounds 1–3

Ion (<i>m/z</i>)	Relative abundance (%)		
	1	2	3
195	—	2	—
194	—	7	—
179	1	—	—
178	9	—	5
177	—	—	38
151	—	3	—
135	4	—	—
134	—	—	5
120	—	—	5
110	—	55	—
109	—	27	—
94	100	—	5
93	—	—	62
85	18	45	5
77	9	5	11
69	1	6	1
65	17	17	13
57	74	100	100
51	5	7	5
41	27	43	27
39	26	22	15

SCHEME – 1

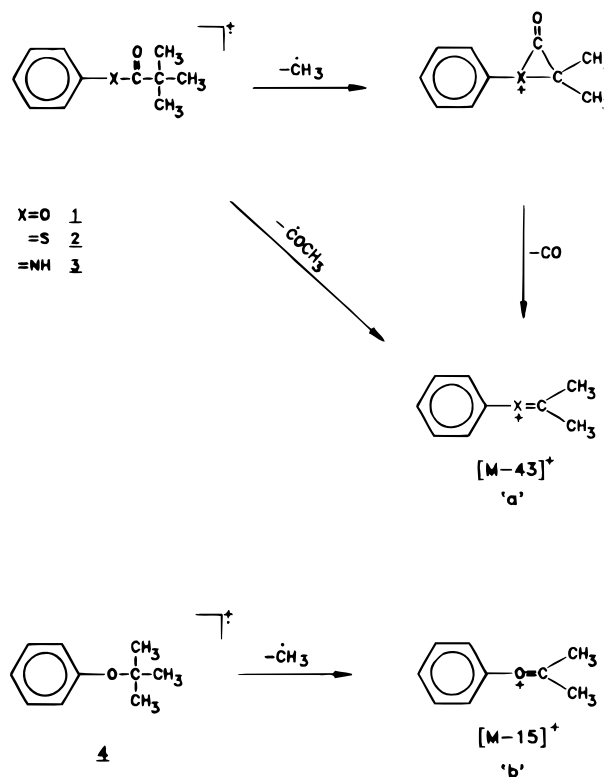


Table 2. CID mass spectra of m/z 135 from compounds 1 and 4

Ion (m/z)	Relative abundance (%)	
	1	4
120	1.9	1.6
119	8.7	3.2
117	3.2	3.5
115	7.4	3.9
108	3.8	3.9
107	100.0	100.0
105	4.8	5.2
103	3.2	1.3
95	73.3	75.8
94	20.7	19.6
92	2.5	1.6
91	21.6	10.4
89	3.2	1.6
79	4.5	3.5
78	3.5	3.9
77	43.5	63.3
76	7.2	11.1
75	3.2	3.9
74	3.2	3.6
65	12.3	9.8
66	4.2	3.9
63	7.1	5.2
62	3.2	1.9
55	3.2	2.9
53	3.8	2.2
51	16.2	20.2
50	8.4	9.8
43	6.8	10.7
41	24.0	20.9
40	3.2	2.7
39	13.3	9.8

Based on these data, the mechanism shown in Scheme 1 can be proposed for the formation of the $[M-43]^+$ ion with all the

compounds. The structure of the $[M-43]^+$ ion *a* in 1 was compared with the structure of the $[M-15]^+$ ion *b* formed from phenyl *tert*-butyl ether (4) by CID studies and the CID spectra are found to be closely similar (Table 2), although not identical.

This result suggests the operation of other mechanisms for the formation of the $[M-43]^+$ ion in addition to the proposed one which may be the major pathway. Further work aimed at elucidating the driving force for the loss of CH_3CO in these compounds is in progress.

P. K. and S. P. thank the UGC and CSIR, New Delhi, respectively, for the award of Junior Research Fellowships.

Yours,

P. KRISHNA, S. PRABHAKAR and M. VAIRAMANI†
Indian Institute of Chemical Technology, Hyderabad-500 007,
India

REFERENCES

1. P. Brown and C. Djerassi, *Angew. Chem., Int. Ed. Engl.* **6**, 477 (1967), and references cited therein.
2. D. H. Williams, R. G. Cooks, J. H. Bowie, P. Madsen, G. Schroll and S. O. Lawesson, *Tetrahedron* **23**, 3173 (1967).
3. M. Vairamani and U. A. Mirza, *Org. Mass. Spectrom.* **22**, 406 (1987).
4. M. Fischer and C. Djerassi, *Chem. Ber.* **99**, 750 (1966).
5. J. H. Bowie, R. G. Cooks, S. O. Lawesson and C. Nolde, *J. Chem. Soc. B* 616 (1967).
6. Y. Rahamim, J. Sharvit, A. Mandelbaum and M. Sprecher, *J. Org. Chem.* **32**, 3856 (1967).
7. M. A. Winnik, *Org. Mass. Spectrom.* **9**, 920 (1974).
8. J. H. Bowie, D. H. Williams, P. Madsen, G. Schroll and S. O. Lawesson, *Tetrahedron* **23**, 305 (1967).
9. D. V. Ramana, M. Vairamani and S. Kala, *Org. Mass Spectrom.* **10**, 196 (1975).

† Author to whom correspondence should be addressed.