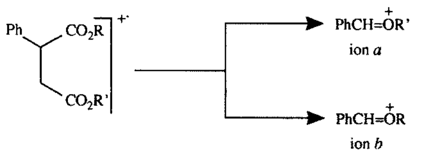
ORGANIC MASS SPECTROMETRY, VOL. 27, 527–528 (1992)

OMS Letters

Dear Sir

The Mechanism of Formation of Alkoxybenzylidene $[PhCH{=}OR]^+$ Ions from Mixed Dialkyl Esters of Phenylsuccinic Acid upon Electron Ionization. Methoxy Group Migration between Two Carbonyl Groups

In a recent publication we have shown that mixed dialkyl esters of phenylsuccinic acid (**1–6**) give rise to two alkoxybenzylidene cations *a* and *b* under electron ionization by sequential elimination of an alkoxy radical, carbon monoxide and ketene (Scheme 1).[1] The formation of ion *a* ($R'{=}CH_3$) was observed a long time ago in the symmetrical dimethyl phenylsuccinate (**7**) and a mechanism involving migration of the 4-methoxy group to the benzylic position has been suggested (Scheme 2). This mechanism explains formation of ions *a* from the unsymmetrical esters **1–6**.

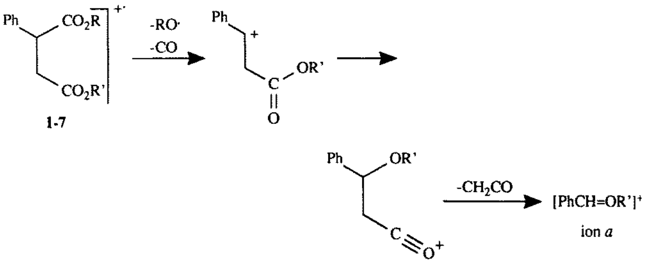


1a R=Me; R'=Et
1b R=Et; R'=Me
2a R=Me; R'=Pr
2b R=Pr; R'=Me
3a R=Me; R'=i-Pr
3b R=i-Pr; R'=Me

4a R=Me; R'=Bu
4b R=Bu; R'=Me
5a R=Et; R'=i-Pr
5b R=i-Pr; R'=Et
6a R=Et; R'=Bu
6b R=Bu; R'=Et

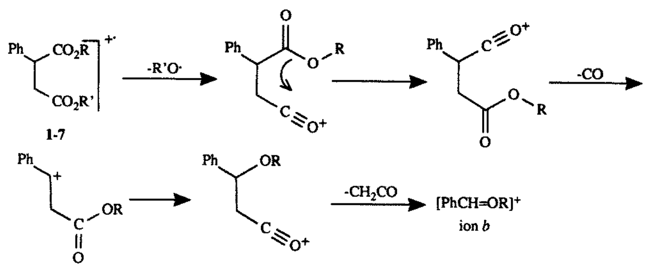
7 R,R'=Me

Scheme 1

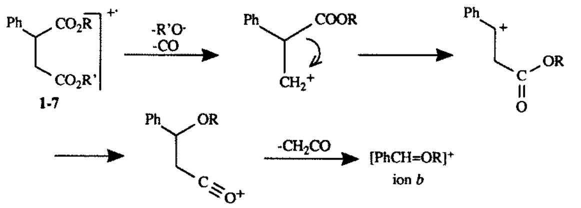


Scheme 2

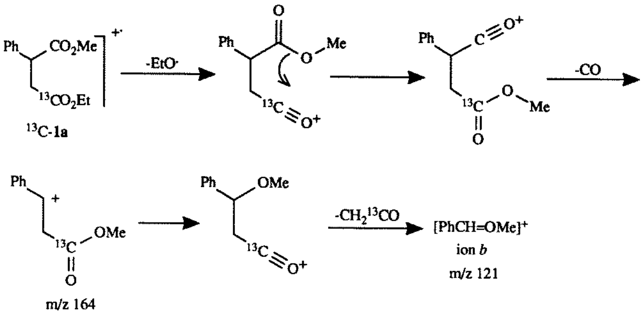
Two possible mechanisms proposed for the formation of ions *b* are shown in Scheme 3 and 4. One (Scheme 3) involves a transfer of RO$^\bullet$ radical from its original site to the other carbonyl group in the $[M - R'O]^+$ ion, followed by elimination of CO (position 1) and ketene. The alternative route (Scheme 4) involves migration of the alkoxycarbonyl group COOR from position 2 to 3 in the $[M - OR' - CO]^+$ ion.



Scheme 3



Scheme 4



Scheme 5

1-Methyl-4-ethyl-2-phenyl-4-^{13}C-succinate (^{13}C-**1a**) and 1-ethyl-4-methyl-2-phenyl-4-^{13}C-succinate (^{13}C-**1b**) were synthesized[2] in order to distinguish between the above two proposed mechanisms. The EI mass spectrum of ^{13}C-**1a** is shown in Fig. 1. The presence of a *m/z* 164 ion and practical absence of a *m/z* 163 ion (taking into account natural abundance of ^{13}C isotope ion of *m/z* 162 $[M - EtOH - {}^{13}CO]^{+\bullet}$) clearly indicates that the loss of $C_2H_5O^\bullet$ radical from position 4 is followed by elimination of the unlabelled CO (position 1). This sequence of events suggests migration of the MeO group from the 1-carbonyl group to the other (position 4) prior to the decarbonylation step (Scheme 5).

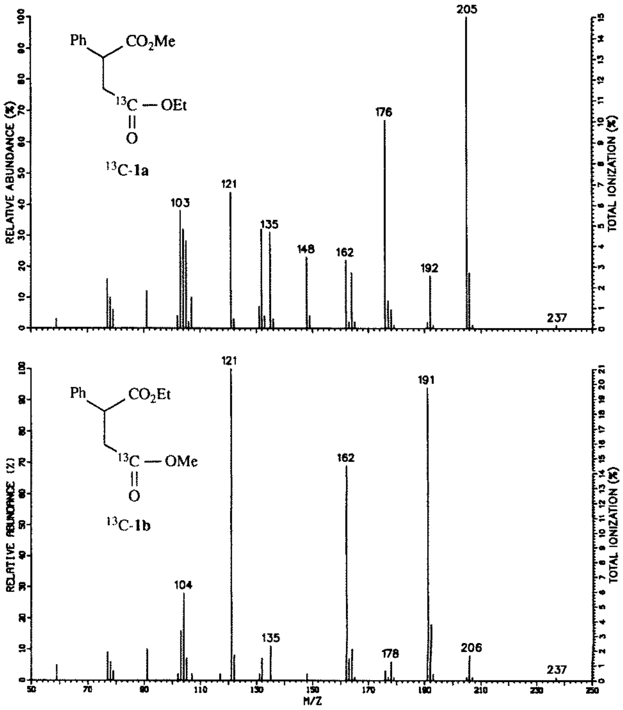


Figure 1. EI mass spectra of ^{13}C-**1a** and ^{13}C-**1b**.

0030–493X/92/040527–02 $05.00

Received 11 February 1992
Accepted 11 February 1992

Similar results were obtained with ^{13}C-**1b**. The *m/z* 178 ion is formed by the loss of $CH_3O^{\cdot}$ from C-1 followed by elimination of ^{12}CO from C-4 which must be preceded by a migration of the $MeO^{\cdot}$ radical from the latter position.

The above results disprove the mechanism shown in Scheme 4 and are in keeping with the pathway suggested in Scheme 3.

Migration of an alkoxyl from an ester group to a carbocation site has been previously reported as a key step in the *fragmentation* of certain substituted esters.[3] We are aware of one recent report of a migration of an alkoxyl between two carbonyl groups.[4] The use of mixed esters and/or specific labelling of one of the carbonyls enables observation of such migrations which may play a role in the fragmentation of organic gas-phase cations containing several esters groups.

Acknowledgements. This work was supported by the Fund for Promotion of Research at the Technion. We thank Mr Jacob Katzir for technical assistance.

Yours

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References

1. I. Vidavsky, A. Mandelbaum, T. Tamiri and S. Zitrin, *Org. Mass Spectrom.* **26**, 287 (1991).
2. ^{13}C-**1a** was prepared by the Wittig reaction of ethoxy-1-^{13}C-carbonylmethylidenetriphenylphosphorane [obtained from ethyl bromo-1-^{13}C-acetate (Cambridge Isotope Laboratories)] and methyl benzoylformate followed by catalytic hydrogenation. ^{13}C-**1b** was obtained (in mixture with ^{13}C-**1a** and the dimethyl and diethyl esters) by trans-esterification of ^{13}C-**1a** with ethanol–methanol mixture. For technical details see Ref. 1.
3. R. G. Cooks and D. H. Williams, *Chem. Commun.* **1967**, 51; R. G. Cooks, J. Ronayne and D. H. Williams, *J. Chem. Soc.* [*C*] **1967**, 2601.
4. M. Corval, A. Harrata and J-P. Morizur, *Org. Mass Spectrom.* **24**, 977 (1989).