ORGANIC MASS SPECTROMETRY, VOL. 26, 287–292 (1991)

Highly Specific Fragmentation Processes of Isomeric Mixed Esters of Phenylsuccinic Acid Under Electron Impact

I. Vidavsky and A. Mandelbaum†
Department of Chemistry, Technion–Israel Institute of Technology, Haifa, Israel

T. Tamiri and S. Zitrin
Israel Police Headquarters, Jerusalem, Israel

Isomeric mixed dialkyl phenylsuccinates, $PhCH(COOR)CH_2COOR'$, undergo a highly specific elimination of ROH under electron impact. A deuterium-labelling study showed that the hydrogen atom from the benzylic position 2 is abstracted in this process. These results suggest the occurrence of a 'hidden' hydrogen migration of the benzylic hydrogen atom to the carbonylic oxygen of the remote ester group, followed by the elimination of ROH from the adjacent ester group with the involvement of that hydrogen. Alkoxyl group migrations resulting in the formation of $[PhCH{=}OR]^+$ and $[PhCH{=}OR']^+$ ions are less specific, although the migration of the remote R'O· is significantly preferred in all the pairs of isomers examined. Mechanisms are suggested for the formation of the two ions.

INTRODUCTION

We have previously shown that mass spectrometry may be highly sensitive in distinguishing between isomeric mixed dialkyl esters differing in the positions of the alkoxyl groups.[1–4] Mass spectrometry seems to be the most practical technique for the identification and structural determination of such closely similar isomers, which exhibit very similar IR and NMR spectra. The entirely different fragmentation pattern of isomeric methyl ethyl halosuccinates under electron impact was the starting point of an investigation which led to the clarification of the mechanism of halogen elimination.[4] The highly specific behaviour of analogous isomeric mixed diesters of substituted succinic, maleic and other dicarboxylic acids on chemical ionization led to the understanding of the role of steric factors in the proton attachment step.[1,2]

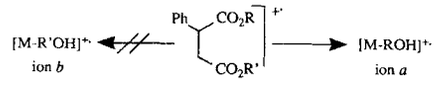
The above examples suggest that close examination of such isomers may be helpful in clarifying subtle mechanistic points which may be otherwise unobserved. We describe here some distinctive features of isomeric mixed esters of phenylsuccinic acid under electron impact (EI) ionization which led to a better understanding of two fragmentation processes in this system.

RESULTS AND DISCUSSION

The isomeric methyl ethyl and ethyl methyl phenylsuccinates **1a** and **1b** give rise to entirely different EI mass spectra (Fig. 1). The most abundant *m/z* 204 ion in the mass spectrum of **1a** arises by elimination of methanol. This ion is almost absent in the mass spectrum of **1b** (relative abundance <1%), which instead eliminates ethanol, resulting in an abundant *m/z* 190 ion. The latter ion is of extremely low abundance (3%) in the mass spectrum of **1a**. The different behaviour of the two isomers **1a** and **1b** is shown in Scheme 1.

Scheme 1

The subsequent fragmentation processes of the $[M - ROH]^{+\cdot}$ ions result in additional differences between **1a** and **1b**. Thus, elimination of C_2H_4 and CO from the *m/z* 204 ion give rise to abundant *m/z* 176 and 148 ions in the mass spectrum of **1a**. These ions are of very low abundance in the mass spectrum of **1b**. Another distinctive feature of the mass spectra of **1a** and **1b** is the pronounced loss of an alkoxyl radical when the elimination of the corresponding alcohol is suppressed. Thus the *m/z* 191 $[M - EtO]^+$ ion is pronounced (although not very abundant, 15%) in the mass spectrum of **1a**, whereas the *m/z* 205 $[M - MeO]^+$ ion is conspicuous in the case of **1b**. Electron impact mass spectra of other isomeric pairs of mixed dialkyl phenylsuccinates **2–6** and the isotopomers **7** indicate the generality of the above distinctive features. In all the materials examined, only one of the two possible alcohols is eliminated, and it originates from the ester group that is adjacent to the phenyl group resulting in the formation of the $[M - ROH]^{+\cdot}$ ion *a* (Scheme 2). The



1-7

Scheme 2

† Author to whom correspondence should be addressed.

0030–493X/91/040287–06 $05.00

Received 18 September 1990
Revised manuscript received 27 November 1990
Accepted 3 December 1990

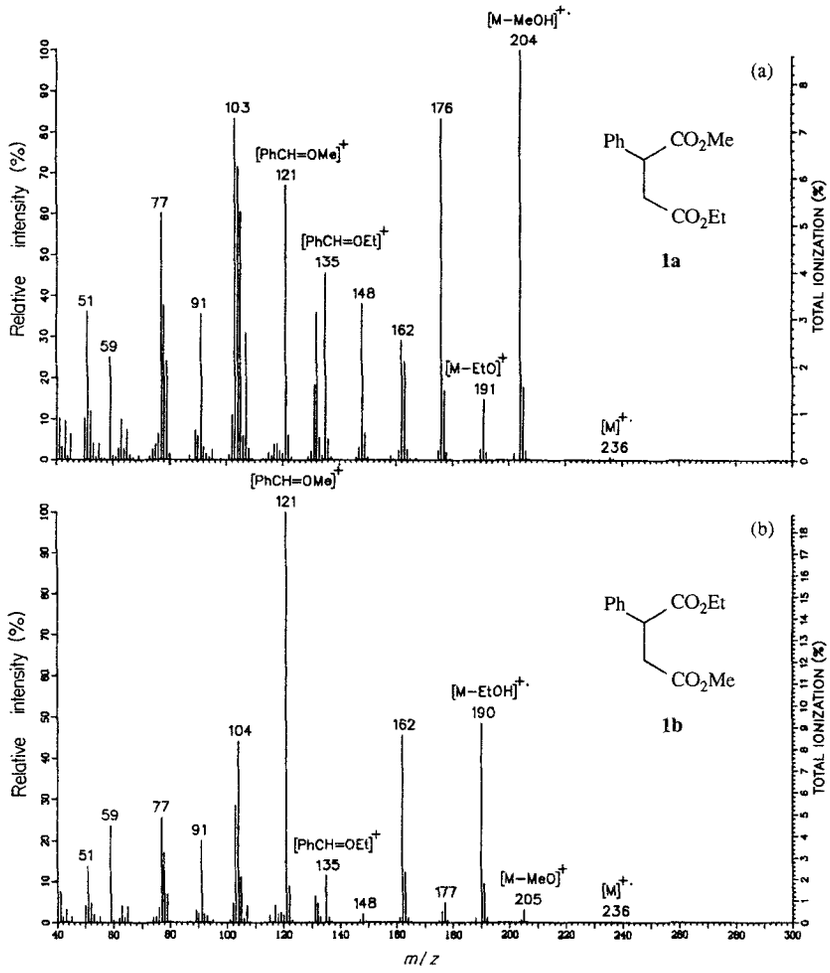


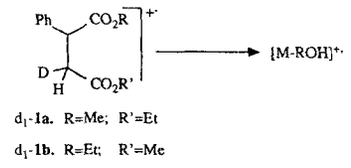
Figure 1. Mass spectra of isomeric methyl ethyl phenylsuccinates: (a) isomer **1a**; (b) isomer **1b**.

relative abundances of the $[M - ROH]^{+\cdot}$ and $[M - R'OH]^{+\cdot}$ ions in the mass spectra of **1–7** are listed in Table 1.

A deuterium-labelling study was undertaken in order to identify the hydrogen atom that is abstracted in the course of elimination of ROH. The isomeric d_3-methyl ethyl and methyl d_5-ethyl phenylsuccinates d_3-**1a**, d_3-**1b**, d_5-**1a** and d_5-**1b** exhibit no elimination of ROD, indicating that no hydrogen from the alkoxyl groups is abstracted in this process (see Table 1).

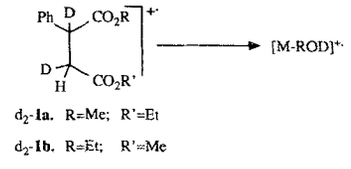
For practical reasons, two pairs of isomers deuterium-labelled at the succinic moiety, d_1-**1** and d_2-**1**, were prepared, with one deuterium atom at positions 3 and with two labels at positions 2 and 3, respectively. The two isomers d_1-**1a** and d_1-**1b** eliminate regular methanol and ethanol, respectively, with full retention of the label in the resulting $[M - MeOH]^{+\cdot}$ and $[M - EtOH]^{+\cdot}$ ions. The other isomeric pair d_2-**1a** and d_2-**1b** exhibit virtually quantitative elimination (>98%) of deuterated methanol and ethanol, respectively, giving rise to $[M - MeOD]^{+\cdot}$ (*m/z* 205, 100% for d_2-**1a** and <1% for d_2-**1b**) and $[M - EtOD]^{+\cdot}$ (*m/z* 191, <1% for d_2-**1a** and 55% for d_2-**1b**) ions (see Scheme 3).

These results clearly show that the benzylic hydrogen atom is abstracted in the course of the highly specific alcohol elimination from dialkyl phenylsuccinates. A plausible mechanism for this process is suggested in Scheme 4. The key step in this mechanism is the 'hidden hydrogen transfer'[5] from the benzylic position to the remote ester group, and it is followed by the elimination step with the abstraction of that hydrogen.



d_1-**1a**. R=Me; R'=Et

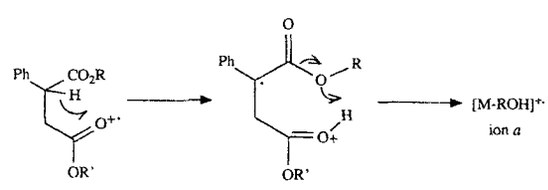
d_1-**1b**. R=Et; R'=Me



d_2-**1a**. R=Me; R'=Et

d_2-**1b**. R=Et; R'=Me

Scheme 3



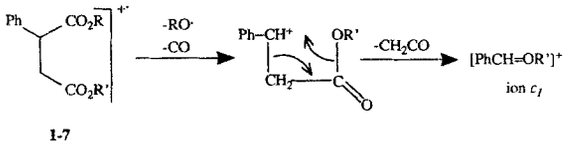
Scheme 4

Table 1. Abundances of ions *a* and *b* in EI mass spectra of isomeric mixed dialkyl phenylsuccinates 1–7.

			[M – ROH]$^{+\cdot}$		[M – R'OH]$^{+\cdot}$	
Compound	R	R'	*m/z*	Relative abundance (%)	*m/z*	Relative abundance (%)
1a[a]	Me	Et	204	100 (93)[b]	190	3 (3)[b]
1b[a]	Et	Me	190	49 (65)[b]	204	<1 (<1)[b]
2a[a]	Me	Pr	218	30	190	4
2b[a]	Pr	Me	190	54	218	<1
3a[a]	Me	i-Pr	218	23	190	3
3b[a]	i-Pr	Me	190	37	218	<1
4a[a]	Me	Bu	232	29	190	2
4b[a]	Bu	Me	190	63	232	<1
5a[a]	Et	i-Pr	218	17	204	<1
5b[a]	i-Pr	Et	204	51	218	<1
6a[a]	Et	Bu	232	35	204	1
6b[a]	Bu	Et	204	100	232	<1
7a[a]	CH_3	CD_3	193	56	190	2
7b[a]	CD_3	CH_3	190	63	193	1.5
d_3-**1a**[b]	CD_3	C_2H_5	204	100	193	2.8
d_3-**1b**[b]	C_2H_5	CD_3	193	54	204	<1
d_5-**1a**[b]	CH_3	C_2D_5	209	100	190	3.5
d_5-**1b**[b]	C_2D_5	CH_3	190	100	209	<1

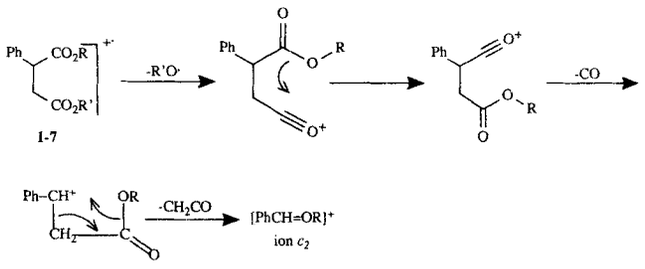
[a] Measured with Finnigan 4500.
[b] Measured with Finnigan TSQ-70B.

An additional difference between the EI mass spectra of **1a** and **1b** appears in the relative abundance of $[C_8H_9O]^+$ (*m/z* 121) and $[C_9H_{11}O]^+$ (*m/z* 135) ions. Metastable transition measurements indicate the formation of these ions by elimination of ketene from the $[M - RO - CO]^+$ ions, which involves migration of an alkoxyl group from an ester function to the benzylic position. These ions are shifted by 1 u to *m/z* 122 and 136 in the mass spectra of the deuterium-labelled analogs d_2-**1**, but remain unchanged in the mass spectra of d_1-**1**. These results clearly indicate that the benzylic hydrogen atom is retained in the two ions. Analogous pairs of ions also appear in the mass spectra of the other isomeric pairs **2–7**. A simple mechanistic pathway for the formation of $[PhCH{=}OR']^+$ (or an isomeric structure) ions c_1 which retain the alkoxyl that is remote from the benzylic position is shown in Scheme 5.

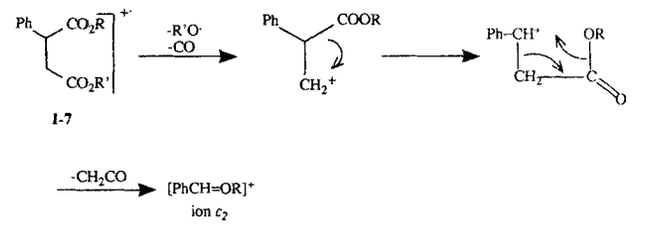


Scheme 5

The competing process leading to ions c_2 which retain the alkoxyl group that is closer to the benzylic position in the original molecule must involve an additional rearrangement step. Two simple pathways for this process are suggested in Schemes 6 and 7. One involves a transfer of the RO· radical from its original site to the other carbonyl group in the $[M - R'O]^+$ ion, followed by elimination of CO and ketene. In the other (Scheme 7), the alkoxycarbonyl group COOR is suggested to migrate[6] from the benzylic position 2 to C(3) in the $[M - R'O]^+$ ion followed by migration of RO· to the benzylic position and subsequent expulsion of ketene.



Scheme 6



Scheme 7

Identification of the origin of the carbonyl group lost in the course of ketene elimination by a specific ^{18}O labelling could distinguish between the two suggested pathways. This investigation is planned for the future. The abundance data for the products of the two competing rearrangements in the isomeric pairs **1–7** are listed in Table 2.

A pronounced difference is observed in the abundances of ions c_1 and c_2 in the mass spectra of the series **1b–6b** having a smaller alkoxyl group R'O at the ester group that is remote from the benzylic position. Ions c_1

Table 2. Abundance data for ions c_1, c_2 and d in the EI mass spectra of isomeric mixed dialkyl phenylsuccinates 1–7

	Ion c_1		Ion c_2		Ion d		
Compound	m/z	RA[a] (%)	m/z	RA[a] (%)	Assignment	RA[a] (%)	RA($c + d$[b])/RA($c' + d$[b])
1a	135	45	121	67	$[c - C_2H_4]^+$	31	1.1
1b	121	100	135	11	$[c' - C_2H_4]^+$	11	4.5
2a	149	20	121	40	$[c - C_3H_6]^+$	17	0.9
2b	121	100	149	8	$[c' - C_3H_6]^+$	7	6.6
3a	149	17	121	42	$[c - C_3H_6]^+$	18	0.8
3b	121	100	149	6	$[c' - C_3H_6]^+$	7	7.7
4a	163	17	121	41	$[c - C_4H_8]^+$	20	0.9
4b	121	100	163	13	$[c' - C_4H_8]^+$	8	4.8
5a	149	15	135	10	$[c - C_3H_6]^+ + [c' - C_2H_4]^+$	24	1.5[c]
5b	135	81	149	13	$[c - C_2H_4]^+ + [c' - C_3H_6]^+$	31	6.2[c]
6a	163	16	135	18	$[c - C_4H_8]^+ + [c' - C_2H_4]^+$	41	0.9[c]
6b	135	76	163	3	$[c - C_2H_4]^+ + [c' - C_4H_8]^+$	39	25[c]
7a	124	100	121	31	—	—	3.2
7b	121	100	124	36	—	—	2.8

[a] RA = relative abundance.
[b] Where applicable.
[c] Abundance ratio of ion c_1/ion c_2.

are considerably more abundant than ions c_2 in these isomers, indicating higher rates for the simpler rearrangement involving migration of the remote alkoxyl (Scheme 5). The abundance of the m/z 107 $[PhCH{=}OH]^+$ ion d obtained by elimination of alkenes from ions c_1 and c_2 having R or R′ groups larger than methyl was added to the abundances of ions c_1 and c_2 (where applicable) in order to ensure more reliable data for comparison in Table 2. The abundance ratios of ions c_1 and c_2 are smaller in the mass spectra of the other series, **1a–6a**, and in four cases they are <1. This behaviour may result from the greater migratory aptitude of the smaller alkoxy groups. The overall abundance of ions c_1 and c_2 in each case is the result of the two effects, namely the preference for formation of ions c_1 and the effect of the size of the alkoxy group on the rate of its migration. The different behaviour within each pair of isomers is clearly demonstrated in their mass spectra.

The isotopomers **7a** and **7b** make it possible to determine the ratio of the rates of formation of ions c_1 and c_2 independent of the group size effect. This ratio is 2.8 in the case of **7a** and 3.2 in **7b**. These results indicate a preference factor of ~ 3 for the formation of ion c_1. They also show the presence of a significant secondary isotope effect in these processes.

The formation of ion c_1 (R′ = Me) has been reported in the case of dimethyl phenylsuccinate.[7] It was explained by the loss of the methoxycarbonyl group attached to the benzylic position, followed by migration of the methoxy group from the other methoxycarbonyl group and subsequent elimination of ketene. This mechanism is identical with that suggested in Scheme 6 for the formation of the more abundant ion c_1. The present results indicate that the reality is more complicated, and a significant portion of these rearrangement ions may result from a more complex process which may be described by pathways such as shown in Schemes 6 and 7.

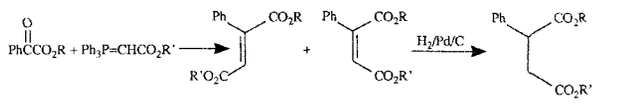
EXPERIMENTAL

Mass spectrometry

High-resolution mass spectra (of **1a**, **1b**, **7a** and **7b**) were measured with a Varian MAT 711 double-focusing mass spectrometer. Gas chromatographic/mass spectrometric analyses were carried out on a Finnigan 4500 quadrupole mass spectrometer (**1–7**) and on a Finnigan TSQ-70B triple-stage quadrupole mass spectrometer (d_3-**1a**, d_3-**1b**, d_5-**1a** and d_5-**1b**). Separations were performed on a DB-5 (0.25 μm film) 15 m × 0.25 mm i.d. capillary column. The column temperature was programmed from 80 to 220 °C at 10 °C min^{-1}. The electron energy was 70 eV and the scan rate 1 s^{-1}. The metastable transition measurements were performed on the Varian MAT 711 mass spectrometer by the acceleration voltage scan technique.

Materials

Compounds **1a**, **1b**, **7a** and **7b** and the isomers labelled in the succinic moiety were synthesized by the Wittig reaction (see Scheme 8). Other pairs of isomers, **2–6**, and analogues labelled in the alkoxyl groups were prepared as mixtures by esterification of phenylsuccinic acid with mixtures of appropriate alcohols, and the structures of the particular isomers were deduced by correlation with



8a. R=Me; R′=Et **9a.** **1a.** R=Me; R′=Et
8b. R=Et; R′=Me **9b.** **1b.** R=Et; R′=Me
10a. R=CH_3; R′=CD_3 **11a.** **7a.** R=CH_3; R′=CD_3
10b. R=CD_3; R′=CH_3 **11b.** **7b.** R=CD_3; R′=CH_3

Scheme 8

1a and **1b** by gas chromatography (isomers **b** had shorter retention times) and mass spectrometry.

1a. A solution of ethoxycarbonylmethylidenetriphenylphosphorane, $Ph_3P{=}CHCO_2Et$,[8] (2.02 g, 5.8 mmol) and methyl benzoylformate (0.92 g, 5.6 mmol) in chloroform (25 ml) was stirred at 15 °C for 20 min. The solvent was evaporated and triphenylphosphine oxide was crystallized out from a solution of hexane and ethyl acetate. The mixture of *Z* and *E* isomers (1 : 2.5 by NMR) was separated by flash chromatography on a column of silica gel (1 : 5 ethyl acetate/hexane solution as eluent), and yielded 4-ethyl-1-methyl 2-phenylfumarate, **8a** (608 mg, 46% yield, pure by thin-layer chromatography (TLC), NMR spectroscopy and gas chromatography/mass spectrometry (GC/MS); ^{1}H NMR: δ = 1.04(t, 3H), 3.78(s, 3H), 4.02(q, 2H), 7.0(s, 1H), 7.3(m, 5H) ppm), and 4-ethyl-1-methyl 2-phenylmaleate, **9a** (242 mg, 18.6% yield, pure by TLC, NMR and GC/MS; ^{1}H NMR: δ = 1.05(t, 3H), 3.67(s, 3H), 3.98(q, 2H), 6.0(s, 1H), 7.2(m, 5H) ppm).

A mixture of **8a** and **9a** (100 mg, 0.43 mmol) was hydrogenated over Pd/10% C in ethanol at room temperature with hydrogen at 1 atm. Evaporation of the solvent yielded **1a** as a colourless oil (99 mg, 98% yield, pure by TLC, NMR and GC/MS); ^{1}H NMR: δ = 1.2(t, 3H), 2.65(dd, 1H), 3.15(dd, 1H), 3.66(s, 3H), 4.1(m, 3H), 7.25(m, 5H) ppm).

1b. Compound **1b** was prepared by the above procedure using methoxycarbonylmethylidenetriphenylphosphorane, $Ph_3P{=}CHCO_2Me$, and ethyl benzoylformate. The mixture of *Z* and *E* isomers (1 : 3 by NMR) was separated (1 : 4.5 ethyl acetate/hexane solution as eluent) and yielded 1-ethyl-4-methyl-2-phenylfumarate, **8b** (51% yield; ^{1}H NMR: δ = 1.3(t, 3H), 3.6(s, 3H), 4.25(q, 2H), 7.0(s, 1H), 7.3(m, 5H) ppm), and 1-ethyl-4-methyl-2-phenylmaleate, **9b** (17% yield; ^{1}H NMR: δ = 1.25(t, 3H), 3.6(s, 3H), 4.25(q, 2H), 6.15(s, 1H), 7.3(m, 5H) ppm).

Hydrogenation of a mixture of **8b** and **9b** yielded **1b** (yield 98%; ^{1}H NMR: δ = 1.2(t, 3H), 2.65(dd, 1H), 3.4(dd, 1H), 3.65(s, 3H), 4.1(m, 3H), 7.25(m, 5H) ppm).

d_1-1a. Compound d_1-**1a** was prepared by a similar procedure but the Wittig reaction was carried out in a 1 : 1 mixture of $CDCl_3$ and EtOD. The reaction yielded 4-ethyl-1-methyl 2-phenyl-3-*d*-fumarate, d_1-**8a** (41% yield; ^{1}H NMR: δ = 1.04(t, 3H), 3.78(s, 3H), 4.02(q, 2H), 7.3(m, 5H) ppm), and 4-ethyl-1-methyl 2-phenyl-3-*d*-maleate, d_1-**9a** (15% yield; ^{1}H NMR: δ = 1.05(t, 3H), 3.67(s, 3H), 3.98(q, 2H), 7.2(m, 5H) ppm).

Compound d_1-**8a** was hydrogenated to give *erythro*-d_1-**1a** (99% yield; ^{1}H NMR: δ = 1.2(t, 3H), 2.65(d, 0.05H, *threo* contaminant), 3.15(d, 0.95H), 3.66(s, 3H), 4.1(m, 3H), 7.25(m, 5H) ppm). Compound d_1-**9a** was hydrogenated to give *threo*-d_1-**1a** (98% yield; ^{1}H NMR: δ = 1.2(t, 3H), 2.65(d, 0.95H), 3.15(d, 0.05H), *erythro* contaminant), 3.66(s, 3H), 4.1(m, 3H), 7.25(m, 5H) ppm). The isotopic composition was determined by mass spectrometry and NMR: d_0- 4%, d_1- 96%. The mass spectra of the *erythro* and *threo* isomers were almost identical.

d_1-1b. Compound d_1-**1b** was prepared by a similar procedure to d_1-**1a**. The reaction yielded 1-ethyl-4-methyl 2-phenyl-3-*d*-fumarate, d_1-**8b** (47% yield; ^{1}H NMR: δ = 1.3(t, 3H), 3.6(s, 3H), 4.25(q, 2H), 7.3(m, 5H) ppm), and 1-ethyl-4-methyl 2-phenyl-3-*d*-maleate, d_1-**9b** (13% yield; ^{1}H NMR: δ = 1.25(t, 3H), 3.6(s, 3H), 4.25(q, 2H), 7.3(m, 5H) ppm). Compound d_1-**8b** was hydrogenated to give *erythro*-d_1-**1b** (97% yield; ^{1}H NMR: δ = 1.2(t, 3H), 2.65(d, 0.05H, *threo* contaminant), 3.4(d, 0.95H), 3.65(s, 3H), 4.1(m, 3H), 7.25(m, 5H) ppm). Compound d_1-**9b** was hydrogenated to give *threo*-d_1-**1b** (98% yield; ^{1}H NMR: δ = 1.2(t, 3H), 2.65(d, 0.95H), 3.4(d, 0.05H, *erythro* contaminant), 3.65(s, 3H), 4.1(m, 3H), 7.25(m, 5H) ppm). The isotopic composition was determined by mass spectrometry and NMR: d_0- 4%, d_1- 96%. The mass spectra of the *erythro* and *threo* isomers were almost identical.

d_2-1a. Compound *threo*-d_2-**1a** was prepared by a similar procedure to **1a** from **8a**, but the hydrogenation was carried out with D_2 in MeOD and yielded *threo*-d_2-**1a** (94% yield; ^{1}H NMR: δ = 1.2(t, 3H), 2.65(s, 0.80H), 3.15(s, 0.20H, *erythro* contaminant), 3.66(s, 3H), 4.1(q, 2H), 7.25(m, 5H) ppm). The isotopic composition was determined by mass spectrometry and NMR: d_0- 0%, d_1- 5%, d_2- 95%.

d_2-1b. Compound *threo*-d_2-**1b** was prepared by a similar procedure to *threo*-d_2-**1a** from **8b** (92% yield; ^{1}H NMR: δ = 1.2(t, 3H), 2.65(s, 0.90H), 3.4(s, 0.10H, *erythro* contaminant), 3.65(s, 3H), 4.1(q, 2H), 7.25(m, 5H) ppm). The isotopic composition was determined by mass spectrometry and NMR: d_0- 0%, d_1- 5%, d_2- 95%.

7a. Compound **7a** was prepared by the above procedure using d_3-methoxycarbonylmethylidenetriphenylphosphorane, $Ph_3P{=}CHCO_2CD_3$, and methyl benzoylformate. The mixture of *Z* and *E* isomers (1 : 3 by NMR), was separated (1 : 5 ethyl acetate/hexane solution as eluent), and yielded 1-methyl-4-d_3-methyl 2-phenylfumarate, **10a** (47% yield; ^{1}H NMR: δ = 3.78(s, 3H), 7.0(s, 1H), 7.4(m, 5H) ppm), and 1-methyl-4-d_3-methyl 2-phenylmaleate, **11a** (16% yield; ^{1}H NMR: δ = 3.93(s, 3H), 6.30(s, 1H), 7.4(m, 5H) ppm).

Hydrogenation of a mixture of **10a** and **11a** yielded **7a** as a colourless oil which solidified on standing (yield 97%; m.p. 58 °C; ^{1}H NMR: δ = 2.64(dd, 1H), 3.19(dd, 1H), 3.66(s, 3H), 4.07(dd, 1H), 7.28(m, 5H) ppm).

7b. Compound **7b** was prepared by the above procedure using methoxycarbonylmethylidenetriphenylphosphorane, $Ph_3P{=}CHCO_2CH_3$, and d_3-methyl benzoylformate. The mixture of *Z* and *E* isomers (1 : 2.6 by NMR), was separated (1 : 5 ethyl acetate/hexane solution as eluent), and yielded 1-d_3-methyl-4-methyl 2-phenylfumarate, **10b** (50% yield; ^{1}H NMR: δ = 3.58(s, 3H), 7.0(s, 1H), 7.4(m, 5H) ppm), and 1-d_3-methyl-4-methyl 2-phenylmaleate, **11b** (19% yield; ^{1}H NMR: δ = 3.77(s, 3H), 6.30(s, 1H), 7.4(m, 5H) ppm).

Hydrogenation of a mixture of **10b** and **11b** yielded **7b** as a colourless oil which solidified on standing (yield 98%; m.p. 58 °C; ^{1}H NMR: δ = 2.64(dd, 1H), 3.19(dd, 1H), 3.65(s, 3H), 4.07(dd, 1H), 7.28(m, 5H) ppm.

Acknowledgements

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

REFERENCES

1. A. Weisz, M. Cojocaru and A. Mandelbaum, *J. Chem. Soc., Chem. Commun.* 331 (1989).
2. A. Mandelbaum, A. Weisz and M. Cojocaru, *Adv. Mass. Spectrom.* **11**, 598 (1989).
3. A. Mandelbaum, D. Bornstein, T. Tamiri and S. Zitrin, 35th ASMS Annual Conference on Mass Spectrometry and Allied Topics, Denver, Colorado, Abstracts, 85, 24–29 May 1987.
4. D. Bornstein, B. Domon, A. Mandelbaum, D. Mueller and W. J. Richter, 34th ASMS Annual Conference on Mass Spectrometry and Allied Topics, Cincinnati, Ohio, Abstracts, 95, 8–13 June 1986.
5. H. Schwarz, *Top. Curr. Chem.* **97**, 1 (1981), and references cited therein; D. Bornstein, A. Weisz and A. Mandelbaum, *Org. Mass Spectrom.* **21**, 225 (1986), and Refs. 9 and 10 therein.
6. A 1,2-migration of protonated alkoxycarbonyl $[ROCOH]^+$ to a radical site has recently been suggested: E. Goeksu, T. Weiske, H. Halim and H. Schwarz, *J. Am. Chem. Soc.* **106**, 1167 (1984); T. Weiske, H. Halim and H. Schwarz, *Chem. Ber.* **118**, 495 (1985).
7. R. G. Cooks and D. H. Williams, *Chem. Commun.* 51 (1967).
8. O. Isler, H. Gutmann, M. Montavon, R. Ruegg and G. Zeller, *Helv. Chim. Acta* **40**, 1242 (1957).