

Chemistry and Stereochemistry of Benzyl–Benzyl Interactions in MH^+ Ions of Dibenzyl Esters upon Chemical Ionization and Collision-induced Dissociation Conditions

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Isobutane chemical ionization mass spectra of dibenzyl esters of a wide variety of aliphatic, olefinic, alicyclic and aromatic dicarboxylic acids exhibit abundant m/z 181 $C_{14}H_{13}^+$ ions, indicating a highly general rearrangement process involving the formation of a new bond between the two benzyl groups. An extensive collision-induced dissociation and deuterium labeling study suggested that these ions are an almost equimolar mixture of isomeric α -*o*-tolylbenzyl, α -*p*-tolylbenzyl and *p*-benzylbenzyl cation structures, and this composition is identical for all the diesters examined. This structural assignment of the $C_{14}H_{13}^+$ ions suggests a mechanistic pathway for their generation, based on the formation of the new bond between the benzyl methylene group of the protonated benzoxy-carbonyl and the phenyl ring of the other ester moiety via π - (and/or ion–neutral) and σ -complexes. Stereoisomeric diesters show an unusual steric effect: *trans*-isomers give rise to much more abundant $C_{14}H_{13}^+$ ions than the *cis* counterparts. This behavior is explained by stabilized proton-bridged structures of the MH^+ ions of the *cis*-isomers.

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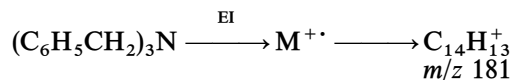
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KEYWORDS: benzyl–benzyl interactions; benzyl esters; rearrangement upon chemical ionization; stereochemical effects; mechanism of fragmentation

INTRODUCTION

Skeletal rearrangements of gas-phase ions have been of great interest since the early days of organic mass spectrometry. One of the early examples of such processes was the formation of a $C_{14}H_{13}^+$ ion from the molecular ion of tribenzylamine under electron impact (EI) ionization, which must involve the formation of a bond between two benzyl groups, which were not connected in the original molecule (Scheme 1).¹ The structure and mechanism of formation of this ion have not been explored in this study.



Scheme 1

Analogous rearrangements leading to the m/z 181 $C_{14}H_{13}^+$ ion were reported later in the EI mass spectra of *N*-nitrosodibenzylamine² and *o*- and *m*-dibenzoylbenzenes.³ In the former case it has been proposed that the benzyl–benzyl C–C bond formation

step occurred in the $[M - H]^+$ ion, resulting in a benzylium structure.²

A similar rearrangement has been observed under chemical ionization (CI) conditions in dibenzyl ether, which gave rise to an abundant m/z 181 ion.⁴ The observation of the m/z 181 ion in the high-pressure CI mass spectral measurements of benzyl acetate has been interpreted in terms of an ion–molecule reaction, involving an initial carbonyl–carbonyl interaction followed by a rearrangement step, wherein a benzyl–benzyl C–C bond formation took place.^{5,6}

We have been interested for a long time in various interactions between functional groups resulting in stereochemical effects in gas-phase ions,^{7,8} and more specifically in proton bridging and proton transfer processes between the protonated and free alkoxycarbonyl groups in MH^+ ions of stereoisomeric diesters under CI conditions.^{9–11} In this context, it was of interest to examine the CI behavior of benzyl esters of dicarboxylic acids, which could be expected to exhibit an analogous benzyl–benzyl interaction. Preliminary measurements showed, that the above rearrangement indeed takes place in such esters under CI conditions, affording abundant m/z 181 ions. The objective of this work was to explore the generality of this behavior, the steric requirements of this rearrangement, the structure of the resulting $C_{14}H_{13}^+$ ion(s) and the mechanism of this process.

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RESULTS AND DISCUSSION

Isobutane CI mass spectra of dibenzyl esters **1–27** of a wide variety of aliphatic, olefinic, alicyclic and aromatic dicarboxylic acids were measured, and the abundant ions in these mass spectra are listed in Table 1. All the mass spectra exhibit abundant m/z 181 ions, suggesting a high degree of generality of the rearrangement process resulting in the $C_{14}H_{13}^+$ ions. Collision-induced dissociation (CID) spectra of the MH^+ ions of diesters **1–27** (listed in Table 2) also exhibit the m/z 181 ion as the major product ions. These ions are the most abundant fragments in the majority of the examined compounds, and in a number of cases (**13–16**) competing processes are negligible or absent in the CI and CID mass spectra, with the exception of the m/z 91 $C_7H_7^+$ ion, which is present in all the spectra. The results of both CI and CID measurements indicate high generality for the rearrangement process of dibenzyl esters leading to the $C_{14}H_{13}^+$ ions.

A related competing rearrangement process results in $[MH - 180]^+$ ions, which are of considerable abundance in the CI and CID mass spectra of many of the diesters examined. These protonated diacid cations are formed by the loss of a neutral $C_{14}H_{12}$ molecule from the MH^+ ions, which also indicates formation of a new bond between the two benzyl groups. Elimination of benzyl alcohol and of dibenzyl ether are additional competing reactions, observed in a large number of the diesters that have been investigated.

Mechanism

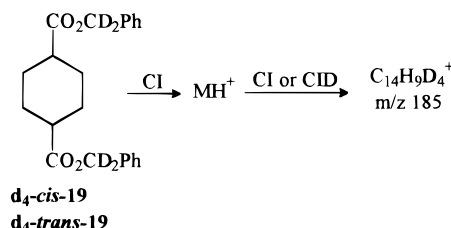
The first point in the search for a mechanism of the rearrangement leading to the formation of the $C_{14}H_{13}^+$

ions in the CI mass spectra of benzyl diesters was to assure structural identity of these ions, when formed from the variety of precursors **1–27**. This goal was achieved by measuring the CID spectra of these m/z 181 ions. The close similarity of the CID spectra indicate identity of the $C_{14}H_{13}^+$ ions obtained from diesters **1–27**.

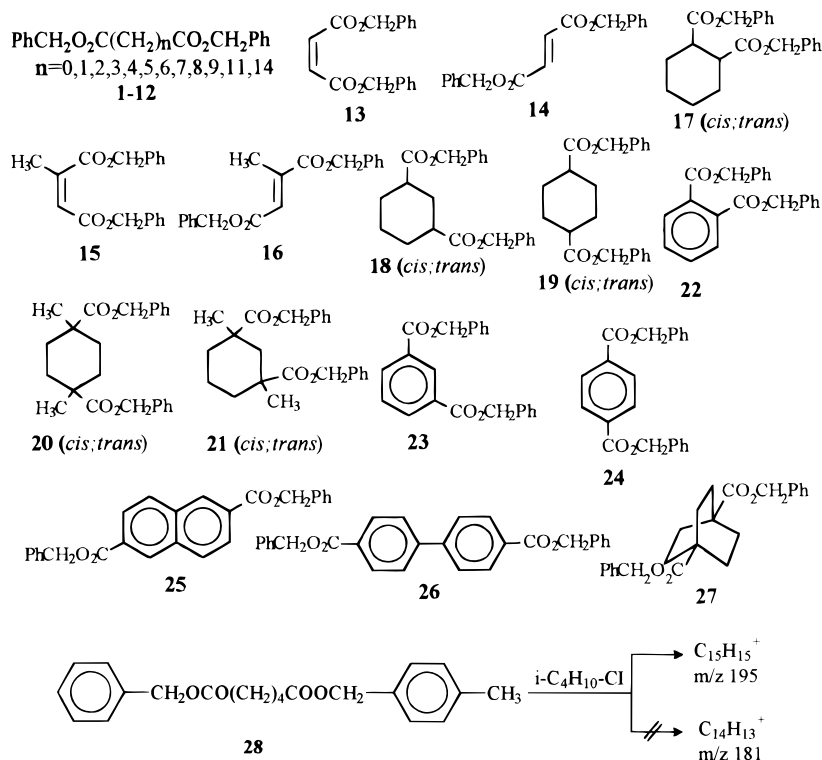
The $C_{14}H_{13}^+$ ion contains all the 14 C atoms of the two benzyl groups, but only 13 H atoms. The question of the origin of the missing fourteenth hydrogen atom could be easily solved by deuterium labeling. The isobutane CI mass spectra of the bis(α,α - d_2 -benzyl) analogues of *cis*- and *trans*-**19** (d_4 -**19**) and the CID spectra of their MH^+ ions clearly indicate exclusive abstraction of a hydrogen atom from one of the phenyl rings in the course of the rearrangement process (Scheme 2). The resulting m/z 185 ions contain all the four benzylic deuterium atoms both under CI and CID conditions.

The exclusively unimolecular nature of the rearrangement under CI conditions was established by examination of the isobutane CI mass spectrum of the mixed benzyl *p*-xylyl diester of adipic acid (**28**) (Scheme 3 and Fig. 1). The exclusive formation of the m/z 195 $C_{15}H_{15}^+$ ion (no m/z 181 ion was detected) clearly indicates the absence of a contribution of an ion–molecule reaction in this process.

Examination of the CID spectra of MD^+ ions, obtained under CD_4 CI and CD_3CN CI conditions,



Scheme 2



Scheme 3

Table 1. Isobutane CI mass spectral data (relative abundance, %) of dibenzyl esters 1–27

Sample	MH ⁺	<i>m/z</i> 181	[MH – 180] ⁺	[MH – PhCH ₂ OH] ⁺	[MH – BnOBn] ⁺
1	2	100	— ^a	<0.1	— ^a
2	47	100	24	<0.1	— ^a
3	50	100	18	2	32
4	70	100	11	34	87
5	56	100	26	32	37
6	13	100	26	38	56
7	21	100	21	32	63
8	5	100	12	13	63
9	7	100	12	17	62
10	8	100	7	22	74
11	3	100	3	8	46
12	2	100	4	0.5	42
13	100	29	— ^a	<0.1	— ^a
14	3	100	— ^a	<0.1	— ^a
15	100	23	— ^a	1	— ^a
16	4	100	— ^a	<0.1	— ^a
<i>cis</i> - 17	100	21	<0.1	40	62
<i>trans</i> - 17	84	63	3	38	100
<i>cis</i> - 18	100	20	<0.1	63	56
<i>trans</i> - 18	13	100	2	2	40
<i>cis</i> - 19	70	100	9	5	16
<i>trans</i> - 19	6	100	15	<0.1	<0.1
<i>cis</i> - 20	28	100	9	40	80
<i>trans</i> - 20	2	100	52	<0.1	<0.1
<i>cis</i> - 21	6	5	<0.1	87	100
<i>trans</i> - 21	<0.1	100	50	<0.1	<0.1
22	100	13	5	8	8
23	2	100	28	5	2
24	2	100	1	6	1
25	<0.1	100	82	<0.1	22
26	7	100	30	6	5
27	3	100	35	2	— ^b

^a The *m/z* values of these fragments are below the range of the CI measurement (>*m/z* 100).

^b The *m/z* value of this fragment (181) coincides with that of the C₁₄H₁₃⁺ ion (second column in this Table).

showed that the external proton (or deuteron) is not transferred to the C₁₄H₁₃⁺ ion in the course of the rearrangement.

A simple mechanistic pathway that may be proposed for the rearrangement, based on anchimerically assisted transfer of a benzyl cation from the protonated benzoxycarbonyl group to the carbonyl oxygen of the other ester group, is shown in Scheme 4. The dibenzoyl carbocation **A** may be expected to afford the *m/z* 181 ion based on precedents discussed in the Introduction. This expectation is supported by the CID spectrum of the *m/z* 241 1,1-dibenzoyl ethyl carbocation **B**, obtained from the dibenzyl ketal of acetone (2,2-dibenzoxyp propane) **29** under EI (Scheme 5). However, the high abundances of the C₁₄H₁₃⁺ ions in the CI mass spectra of *trans*-**19**, *trans*-**20**, *trans*-**21**, **24**, **25**, **26** and **27**, where the distances between the carbonyl oxygen of one benzoxycarbonyl group and the benzylic C atom of the other are large, are inconsistent with this mechanism. Anchimeric assistance is sensitive to the distance between the internal nucleophile and the positive center of the substitution.^{7,12,13}

The distance between the two benzylic C atoms of the benzoxycarbonyl groups in *trans*-**19**, *trans*-**20**, *trans*-**21**, **24**, **25**, **26** and **27** is also too large to allow bond formation between these two carbon atoms leading to ion **a** via the mechanism shown in Scheme 6. Comparison of the CID spectrum of the C₁₄H₁₃⁺ ion obtained by the rearrangement from *cis*- and *trans*-**19** (Fig. 2) with that obtained from 1-bromo-1,2-diphenylethane (**30**) upon isobutane CI (Fig. 3) is also incompatible with this mechanism. These two CID spectra exhibit entirely different dissociation patterns, clearly showing that the C₁₄H₁₃⁺ ion, obtained from dibenzyl esters by the rearrangement process, does *not* have the structure of 1,2-diphenylethyl carbocation (ion **a**), which is obtained by C—Br bond cleavage from **30** (see Scheme 7). This mechanism is also inconsistent with the above results of measurements of bis(α,α -d₂-benzyl) esters *d*₄-*cis*-**19** and *d*₄-*trans*-**19**.

Inspection of molecular models as well as semi-empirical calculations¹⁴ show that interaction between the two phenyl groups in the MH⁺ ions of dibenzyl esters is sterically possible even in **25**, **26** and **27**, where

Table 2. CID^a mass spectral data^{b,c} of MH⁺ ions obtained from dibenzyl esters upon CI

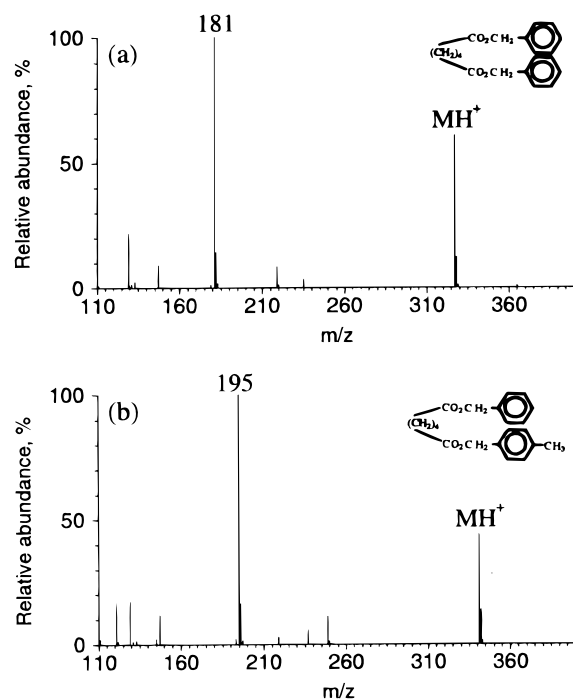
Sample	<i>m/z</i> 181	[MH-180] ⁺	[MH-PhCH ₂ OH] ⁺	[MH-BnOBn] ⁺	<i>m/z</i> 91
1	38.3	— ^d	<0.1	<0.1	50.6
2	42.1	3.8	<0.1	<0.1	54.1
3	54.3	2.3	2.1	<0.1	41.3
4	38.5	3.3	5.7	3.4	49.1
5	53.1	3.2	3.7	2.8	35.2
6	58.7	5.5	0.3	2.9	31.5
7	74.5	0.8	<0.1	5.7	10.6
8	52.7	1.5	<0.1	8.1	31.2
9	45.1	21.7	<0.1	14.7	13.9
10	57.6	6.9	4.0	8.9	12.0
11	53.6	<0.1	<0.1	36.1	3.5
12	62.1	<0.1	<0.1	14.4	6.8
13	31.7	3.8	<0.1	<0.1	64.5
14	55.7	0.4	<0.1	<0.1	33.9
15	35.3	3.0	1.9	1.6	53.9
16	55.6	1.0	<0.1	<0.1	28.6
<i>cis</i> - 17	35.0	0.7	35.0	3.9	40.9
<i>trans</i> - 17	38.0	2.9	26.8	9.1	23.2
<i>cis</i> - 18	10.3	0.1	55.5	1.5	32.6
<i>trans</i> - 18	66.5	1.4	1.6	10.6	19.9
<i>cis</i> - 19	59.8	1.5	3.7	5.9	29.2
<i>trans</i> - 19	81.5	8.7	<0.1	<0.1	<0.1
<i>cis</i> - 20	36.1	1.0	32.9	5.4	14.3
<i>trans</i> - 20	41.9	22.4	<0.1	<0.1	11.9
<i>cis</i> - 21	<0.1	<0.1	88.9	<0.1	11.1
22	22.0	2.1	16.4	2.6	54.1
26	42.0	10.4	6.2	1.2	22.5
27	44.8	10.0	1.8	— ^e	25.0

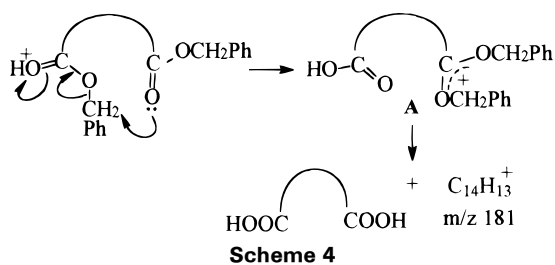
^a 30 eV collision energy.^b The ion abundances are listed as percentages of the total product ion current (%Σ).^c CID spectra of *trans*-**21**, **23**, **24** and **25** were not measured because of low abundance or absence of MH⁺ ions in the isobutane CI mass spectra.^d The *m/z* value (91) of this fragment coincides with the C₇H₇⁺ ion (last column in this Table).^e The *m/z* value (181) of this fragment coincides with the C₁₄H₁₃⁺ ion.

the two benzyloxycarbonyl groups are most distant. Such an interaction could lead to formation of isomeric tolylbenzyl cations **b** (Scheme 8). Here again, CID study involving the three isomeric α -bromoditolyls **31–33** disproves this proposed pathway. The CID spectra of the *m/z* 181 [M – Br]⁺ ions, obtained upon isobutane CI from **31–33** (Fig. 4), show different fragmentation patterns than that of the C₁₄H₁₃⁺ ion obtained by rearrangement of dibenzyl esters (compare Fig. 2).

The failure of the above two attempts to propose a mechanistic pathway for the rearrangement of dibenzyl esters, based on interaction between the two benzylic methylenes and between the two phenyl rings, leaves the third possibility, i.e. interaction of the benzylic C atom of one benzyl group with the phenyl ring of the other, as the basis of the mechanism of formation of the C₁₄H₁₃⁺ ion from the diesters upon CI. Such a pathway would result in one or more of the six possible isomeric α -tolylbenzyl and benzylbenzyl cation structures **c–h** shown in Scheme 9 for the *m/z* 181 C₁₄H₁₃⁺ ion(s). CID spectra were measured for the *m/z* 181 ions obtained by isobutane CI-induced fragmentation of the six isomeric benzylbenzyl alcohols **34–36** and α -tolylbenzyl alcohols **37–39** in order to solve this structural problem.

The CID spectra of the *m/z* 181 ions obtained from the six model compounds **34–39** are shown in Fig. 5.

**Figure 1.** Isobutane CI mass spectra of (a) dibenzyl adipate (**5**) and (b) mixed benzyl *p*-xylyl diester of adipic acid (**28**).



The CID spectra exhibit qualitative similarity, but they show significant, although not large, differences in the relative abundances of the product ions. The spectra of the m/z 181 ions obtained from the two *ortho*-alcohols **34** and **37** are identical, suggesting an identical structure. The lower heat of formation of ion **f** [227.9 kcal mol⁻¹ (1 kcal = 4.184 kJ), calculated by AM1] than that of ion **c** (238.5 kcal mol⁻¹) suggests structure **f** for the ion obtained from both **34** and **37**.

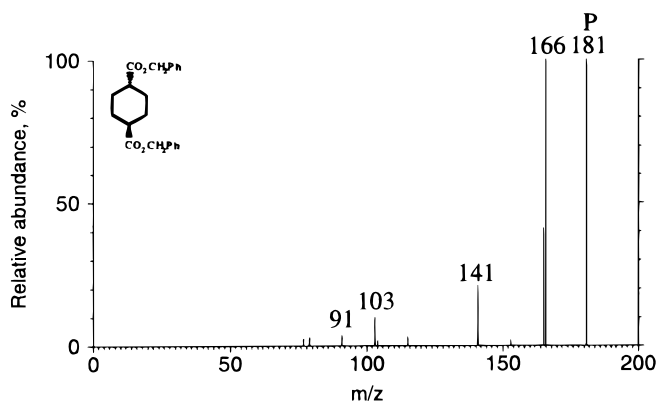


Figure 2. CID spectrum (50 eV collision energy, relative ion abundances (%) normalized to the most abundant product ion) of the m/z 181 $C_{14}H_{13}^+$ ion, obtained by rearrangement from *trans*-**19**.

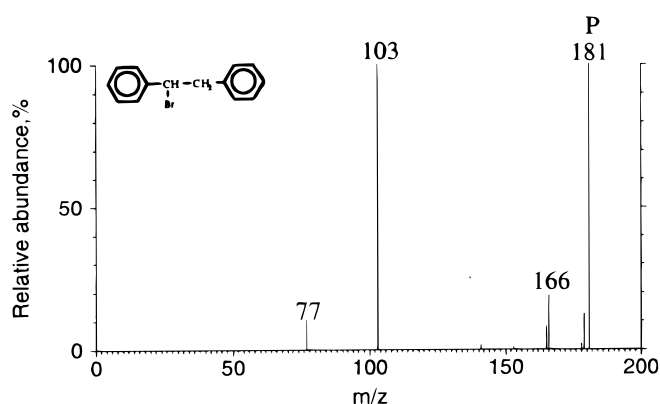
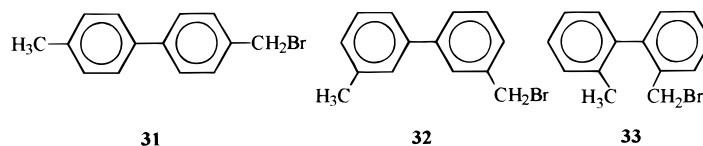
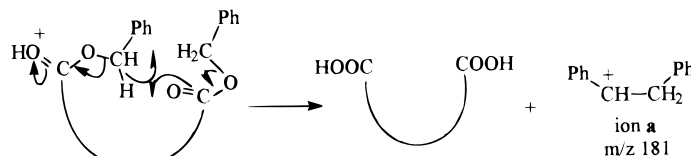
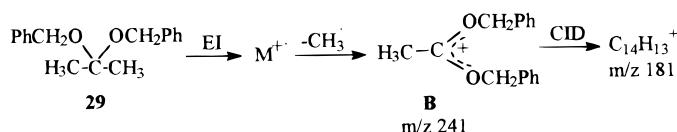
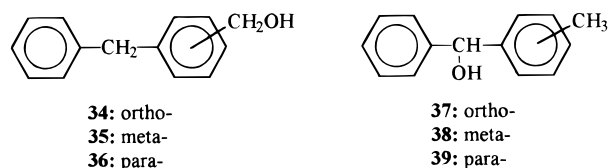
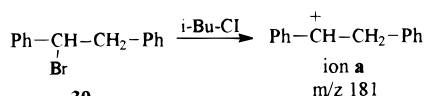


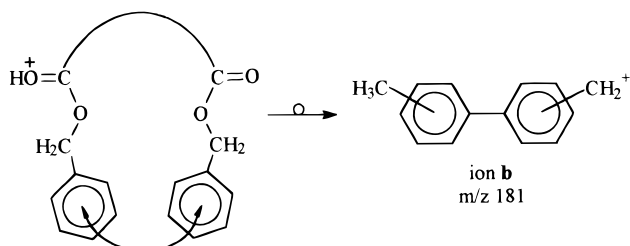
Figure 3. CID spectrum (50 eV collision energy, relative ion abundances (%) normalized to the most abundant product ion) of the m/z 181 $[M - Br]^+$ ion, obtained upon isobutane CI from 1-bromo-1,2-diphenylethane (**30**).

Visual comparison of the CID spectra of the $C_{14}H_{13}^+$ ion obtained by rearrangement of the dibenzyl esters (e.g. of *trans*-**19**, see Fig. 2) with those of **34**–**39** shows qualitative similarity, but no single spectrum of the six model compounds indicated identity with that of the ion in question. A computer-aided analysis has been performed in order to determine an optimum combination of CID data of the models that would fit the CID spectrum of the rearrangement product. The latter spectrum (see Fig. 2) is superimposable with that of the calculated CID spectrum of a mixture of three $C_{14}H_{13}^+$ ions **e** (35%), **f** (35%) and **h** (30%), shown in Fig. 6. The structural conclusion of this analysis is shown in Scheme 10.





Scheme 7

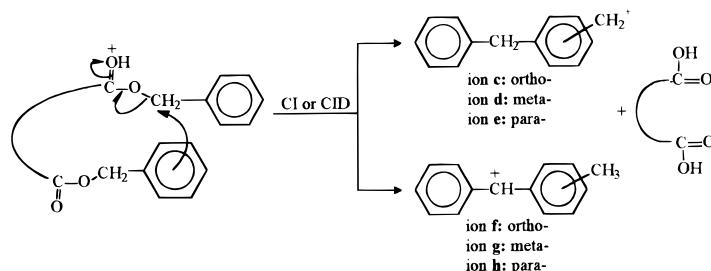


Scheme 8

A plausible mechanism proposed for the rearrangement process, based on the above analysis of the CID spectra, is outlined in Scheme 11. The initial step in this mechanism is the transfer of the benzyl group from the protonated benzoxy carbonyl moiety to the phenyl ring of the other ester group, resulting in the intermediate benzyl π -complex **C**.^{15–20} The formation of the π -complex **C** may be preceded by an ion–neutral complex^{21–24} shown in Scheme 12. The contribution of the ion–neutral complex may be of particular importance in cases where the distance between the two benzoxy carbonyl groups is large. The π -complex **C** rearranges to a mixture of two σ -complexes **D**₁ and **D**₂ with the benzyl substituent at the *ortho* and *para* positions, which in turn undergo proton transfer from the benzenium moieties to the carbonyl oxygen atoms, possibly with the intermediacy of the proton π -complexes **E**₁ and **E**₂ (at least in **D**₁, where the hydrogen atom is at position 4 relative to the ester moiety). The σ -complexes **D**₁ and **D**₂ may be directly formed from the above ion–neutral complex.

An additional hydrogen migration is necessary to afford the α -(*o*-tolyl)- and α -(*p*-tolyl)benzyl cations **f** and **h**. A mechanistic pathway for the formation of ion **f** is proposed in Scheme 13. Formation of ion **h** requires an additional rearrangement step, probably involving intermediacy of another proton π -complex.

Semi-empirical calculations (AM1) indicate significantly different enthalpies of formation for the three product ions of the rearrangement: highest for *p*-benzylbenzyl cation **e** (236.1 kcal mol^{–1}), lower for α -(*o*-tolyl)benzyl ion **f** (227.9 kcal mol^{–1}) and lowest for α -(*p*-tolyl)benzyl ion **h** (222.1 kcal mol^{–1}). Formation of mixture of these three ions under CI conditions indicates the presence of an energy barrier, which does not allow rearrangement to the most stable structure **h** in the time regime of the mass spectral experiment.



Scheme 9

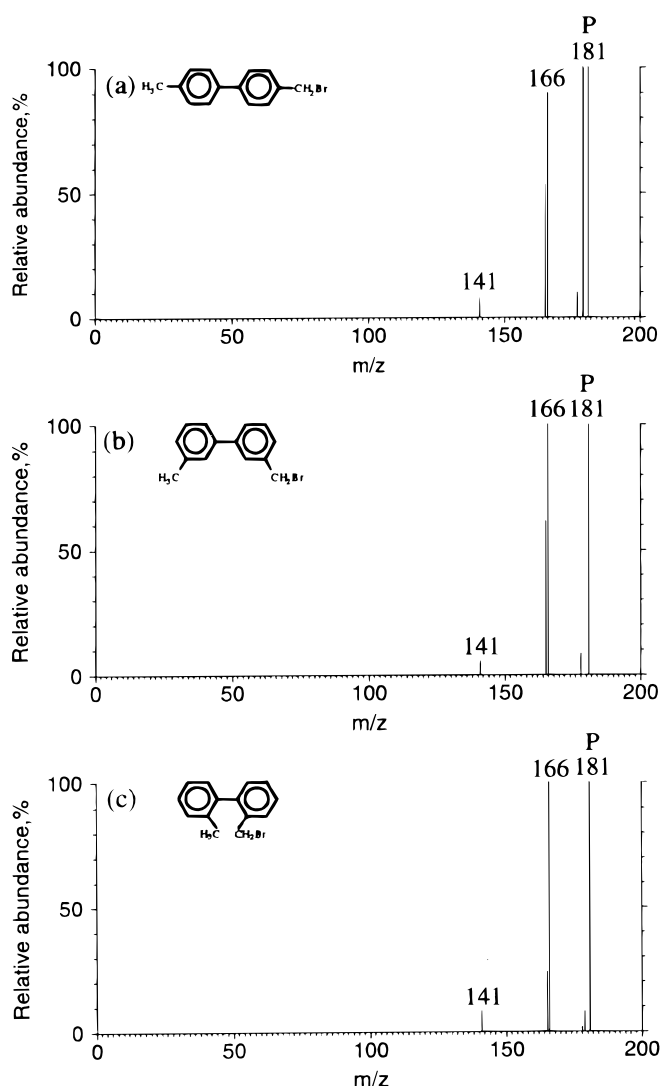


Figure 4. CID spectra (50 eV collision energy, relative ion abundances (%) normalized to the most abundant product ion) of the m/z 181 $\text{C}_{14}\text{H}_{13}^+$ ions obtained upon isobutane CI from (a) **31**, (b) **32** and (c) **33**.

The intermediacy of the benzyl π -complex **C** and/or possibly the ion–neutral complex in the mechanism of formation of ions **e**, **f** and **h** from benzyl diesters (Schemes 11 and 12) finds support in the behavior of the di-2,4,6-trimethylbenzyl esters *cis*- and *trans*-**40**. The low thermal stability of these esters did not allow the measurement of their CI mass spectra, and fast atom bombardment (FAB) ionization was used to obtain their MH^+ ions. The relatively low abundance m/z 265 $\text{C}_{20}\text{H}_{25}^+$ ion observed in the CID spectra of the MH^+

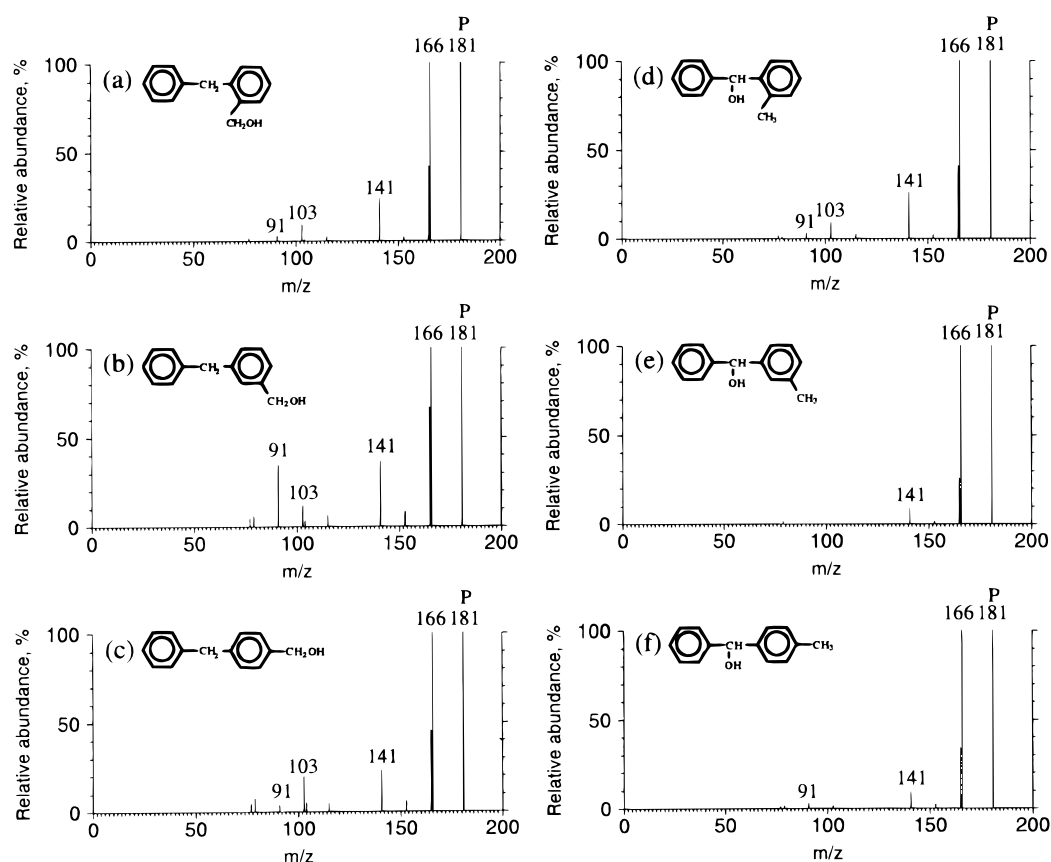


Figure 5. CID spectra (50 eV collision energy, relative ion abundances (%) normalized to the most abundant product ion) of the m/z 181 $C_{14}H_{13}^+$ ions obtained upon isobutane CI from (a) **34**, (b) **35**, (c) **36**, (d) **37**, (e) **38** and (f) **39**.

ions of **40** indicates the operation of a rearrangement process analogous to that of dibenzyl esters, despite the expected steric effect of the methyl groups at positions 2 and 6. The occurrence of the rearrangement in the MH^+ ions of **40** suggests the intermediacy of an ion-neutral complex or of π -complex **F**, which should be undisturbed by the six methyl groups, and should result in the σ -complex **G** by substitution at the *meta* position, leading to the m/z 265 $C_{20}H_{25}^+$ ion **i** (Scheme 14). The

preference for a π - over a σ -complex in sterically hindered systems has been proposed previously.^{15–17}

Stereochemistry of the rearrangement

The $C_{14}H_{13}^+$ rearrangement ions are major fragment ions under CI and CID conditions also in dibenzyl esters with remote benzyloxycarbonyl groups, such as *trans*-**19**, *trans*-**20**, *trans*-**21**, **24**, **25**, **26** and **27** (see Tables 1 and 2). It has been stated above that interaction between the two benzyl groups in the MH^+ ions of

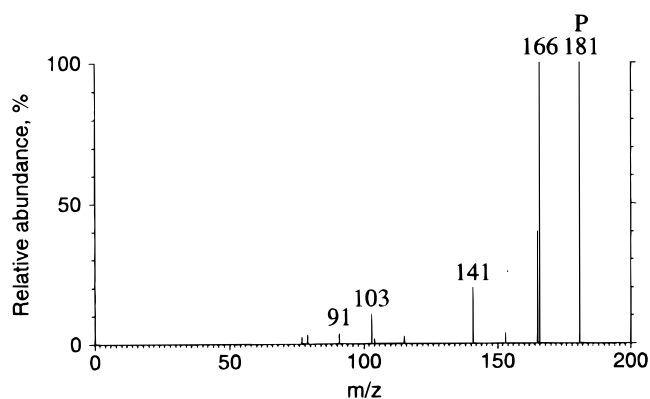
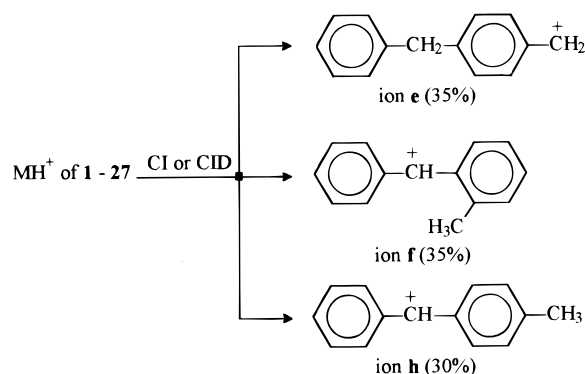
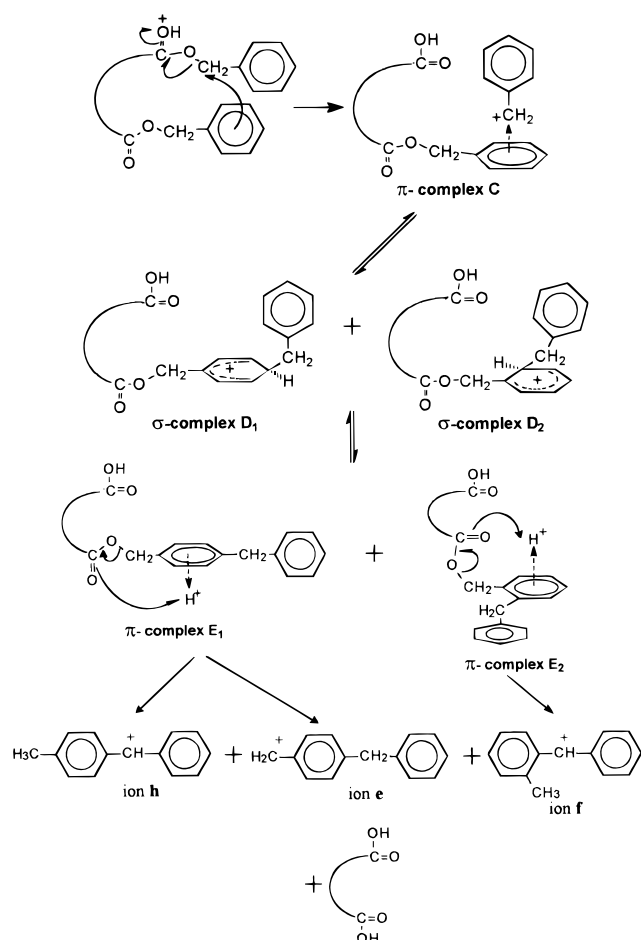


Figure 6. Calculated CID spectrum of a mixture of the three $C_{14}H_{13}^+$ ions **e** (35%), **f** (35%) and **h** (30%) (see text and Scheme 10).



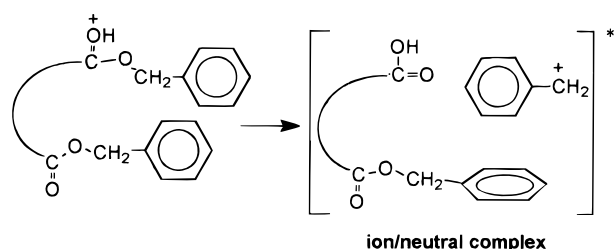
Scheme 10



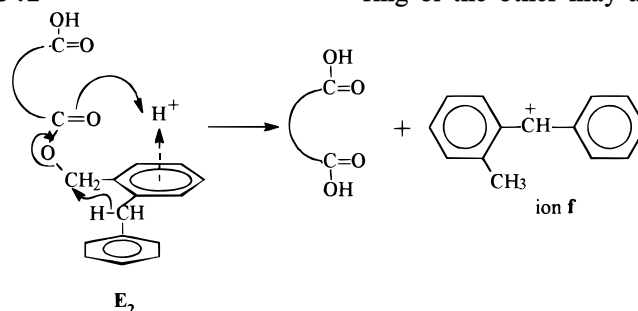
Scheme 11

dibenzyl esters is sterically possible even in **25**, **26** and **27**, where the two benzoxy carbonyl groups are most distant. Therefore, the ready occurrence of the rearrangement in these diesters is in keeping with the mechanism proposed in Scheme 11.

Examination of the CI and CID data of the stereoisomeric pairs of esters **13–14**, **15–16**, *cis*- and *trans*-**18**, **-19**,



Scheme 12



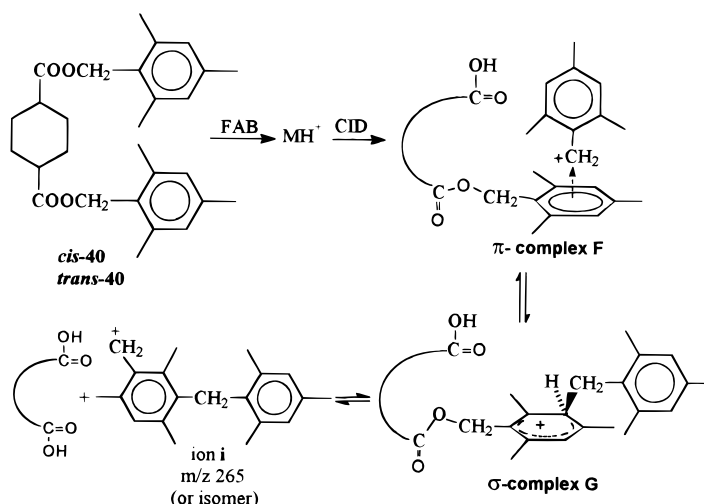
Scheme 13

-20 and **-21** (in Tables 1 and 2) leads to a surprising observation: the rearrangement process of the *trans*-diesters with the remote benzoxy carbonyl groups results in more abundant $C_{14}H_{13}^+$ ions than that of the *cis*-isomers, where the distance between the two interacting ester groups is small. This behavior differs from that of alcohol elimination from MH^+ ions of stereoisomeric methyl and ethyl diesters, which also requires interaction between the two alkoxy carbonyl groups (proton transfer precedes the elimination step), and where only the *cis*-isomers give rise to abundant $[MH - ROH]^+$ ions.⁹ It is also remarkable that the relative abundances of the rearrangement ions increase with the length of the chains of 1, ω -alkanedioic esters **1–12** in their isobutane CI and CID mass spectra.

The relative abundances of the MH^+ ions in the CI mass spectra of all *cis*-diesters are significantly higher than those of the *trans*-isomers (see Table 1). This observation indicates higher stability of the MH^+ ions of the *cis*-isomers, which may result from the internal proton bridged structures **H** and **I**, shown in Scheme 15.

In systems **18–21**, other fragmentation processes, such as elimination of benzyl alcohol and of dibenzyl ether from the MH^+ ion, compete with the rearrangement affording the $C_{14}H_{13}^+$ ion (see Tables 1 and 2). The former two processes involve the formation of new H—O and benzyl—O bonds respectively, which also require interaction between the two ester groups. However, the spatial requirements of these two elimination processes differ from that of the rearrangement leading to the $C_{14}H_{13}^+$ ion: The elimination of alcohols from MH^+ ions of diesters takes place via proton bridged intermediates of the type of ion **H**, which may be formed only when the inter-functional distance is small,⁹ and it may be expected that a similar requirement controls the elimination of dibenzyl ether.

The competition between the three fragmentation processes in the *cis*-isomers might explain the unusual steric effect in formation of the $C_{14}H_{13}^+$ ions in the stereoisomeric pairs *cis*- and *trans*-**18**, **-19**, **-20** and **-21**, but not in **13–14** and **15–16**, where the above processes are unimportant or not observed at all (both under CI and CID conditions, see Tables 1 and 2), and the rearrangement affording the $C_{14}H_{13}^+$ ions is the only dissociation channel in the *cis*- and *trans*-isomers (except for formation of the m/z 91 $C_7H_7^+$ ion, by a simple C—O bond cleavage). Stabilization of the MH^+ ions of the *cis*-diesters by intramolecular proton bridging, shown in Scheme 14, may be the cause of the suppressed rearrangement in these isomers. The distance between the benzyl methylene of one ester group and the phenyl ring of the other may also play a role in lowering the



abundance of the $C_{14}H_{13}^+$ ions in the CI mass spectra of the *cis*-diesters.

CONCLUSION

The results of this study have established a highly general rearrangement process of benzyl esters of dicarboxylic acids, giving rise to very abundant $C_{14}H_{13}^+$ ions under CI and CID conditions. This rearrangement involves an unusual long distance interaction between the two reacting benzyloxycarbonyl groups, affording highly abundant m/z 181 ions in systems with remote ester moieties, such as **24**, **25**, **26** and **27**. The proposed mechanism of this process explains this unusual feature.

It is noteworthy that the isomeric $C_{14}H_{13}^+$ ions **a–h** investigated afford distinguishable CID spectra (with the exception of ions **c** and **f**), indicating the non-occurrence of isomerization to common structure(s) under isobutane CI conditions. This behavior suggests retention of the benzylic nature of these ions rather than transformation to substituted tropylium structures.

EXPERIMENTAL

Mass spectrometry

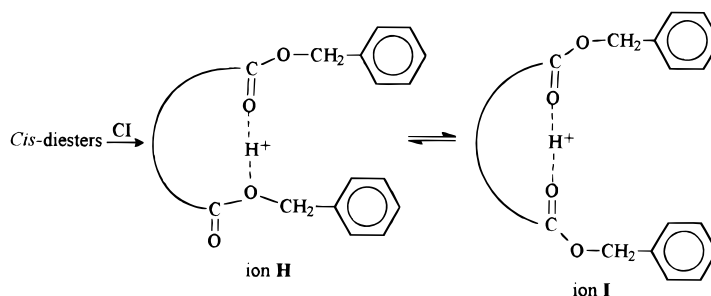
The gas chromatographic/mass spectrometric (GC/MS) analyses and CID measurements were carried out on a

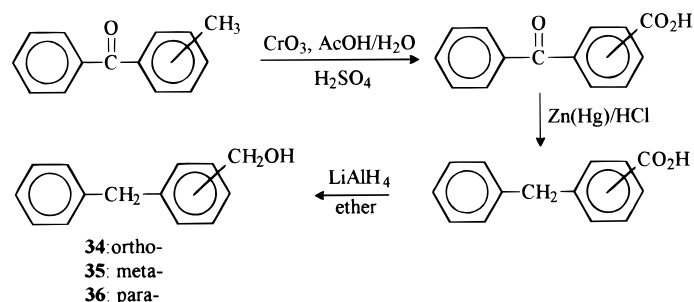
Finnigan TSQ-70B triple-stage quadrupole mass spectrometer. The stereoisomeric pairs were introduced as mixtures, and separations were performed on a DB-5 (0.25 μ m film thickness) 30 m $\times$ 0.25 mm i.d. capillary column at 110 $^{\circ}$ C (isothermal). The scan rate was 1 scan s^{-1} . The elution sequence for the stereoisomers in the GC/MS analyses was as follows: **18t** followed by **18c**, **19c** by **19t**, **20t** by **20c** and **21c** by **21t**. CI measurements were performed at 150 $^{\circ}$ C ion source temperature and 0.4 Torr (indicated) (1 Torr = 133.3 Pa) reagent gas pressure (isobutane, methane, d_3 -acetonitrile). CID measurements were performed with argon as the target gas (0.3 mTorr, indicated) at 30 and 50 eV collision energies (indicated). All CID data used for structural assignments (presented in Figs 2–5) are average of five measurements, and were obtained on a single day under identical conditions in order to assure reliable comparisons.

Materials

Benzyl diesters **1–19**, **22–24** and **27** were prepared by esterification of the corresponding dicarboxylic acids or anhydrides with benzyl alcohol (neat or in toluene solution) in the presence of catalytic amounts of *p*-toluenesulfonic acid (PTSA). Commercial diacids and anhydrides (except 1,4-bicyclo[2.2.2] octanedicarboxylic acid, which was synthesized by a previously reported procedure²⁵) were used in the syntheses.

Deuterium-labeled diesters (d_4 -*cis*-**19** and d_4 -*trans*-**19**) were prepared by the above procedure, using *cis*- and *trans*-cyclohexane-1,4-dicarboxylic acids and α - d_2 -





Scheme 16

benzyl alcohol, obtained by reduction of methyl benzoate with LiAlH_4 .

Dibenzyl esters **20**, **21**, **25** and **26** were obtained by *trans*-esterification of the corresponding methyl diesters with benzyl alcohol in the presence of PTSA (*cis*- and *trans*-1,4- and 1,3-dimethyl-1,4- and 1,3-bis(methoxycarbonyl)cyclohexanes were prepared by methylation of the methyl analogs of *cis*- and *trans*-**18** and **19** with iodomethane and lithium diisopropylamide in tetrahydrofuran²⁶).

Di-2,4,6-trimethylbenzyl esters *cis*- and *trans*-**40** were prepared by acylation of 2,4,6-trimethylbenzyl alcohol with the corresponding acid dichlorides in the presence of 4-*N,N*-dimethylaminopyridine (DMAP) in toluene.^{27,28} 2,4,6-Trimethylbenzyl alcohol was obtained by reduction of mesitoic acid²⁹ with LiAlH_4 .

The synthetic procedure^{30,31} used for preparation of isomeric benzylbenzyl alcohols **35** and **36** is outlined in Scheme 16.

Isomeric α -tolylbenzyl alcohols **37–39** were synthesized by Grignard reaction of phenylmagnesium bromide with the corresponding tolualdehydes.

Isomeric α -bromoditolyls **31–33** were prepared by bromination of 4,4'-, 3,3'- and 2,2'-dimethylbiphenyls with *N*-bromosuccinimide (NBS).³²

1-Bromo-1,2-diphenylethane (**30**) was prepared from 1,2-diphenylethane by NBS bromination.³²

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