Unusual Fragmentation of 1,1,2,2,3,3-Hexamethylindan. Methyl Group Equilibration and Multi-step Skeletal Rearrangements in the [M − CH$_3$]$^+$ Ions Prior to the Formation of t-C$_4$H$_9$$^+$ and Other Fragment Ions[†]

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Based on the surprising observation of an intense C$_4$H$_9$$^+$ (m/z 57) peak in the electron impact mass spectrum, the fragmentation of 1,1,2,2,3,3-hexamethylindan (2) was studied by mass-analysed ion kinetic energy spectrometry of its deuterium-labelled analogues. While methyl loss from ions [2]$^{+\cdot}$ occurs with high selectivity (92%) from the positions 1 and 3 without any rearrangement, ions [2 − CH$_3$]$^+$ undergo complete equilibration of the five methyl groups as intact entities. Subsequent multi-step skeletal rearrangement of the [2 − CH$_3$]$^+$ ions leads to formation of $tert$-butyl ions and to the loss of isobutene and propene, again without concomitant hydrogen exchange. Several kinetic isotope effects and also probably a thermodynamic isotope effect associated with each of these fragmentation processes have been found and their origin is discussed. The possibility of the formation of ion–neutral complexes [t-C$_4$H$_9$$^+$ C$_{10}$H$_{10}$] and [s-C$_3$H$_7$$^+$ C$_{11}$H$_{12}$] is considered on the basis of the labelling and reactivity pattern.

INTRODUCTION

Mass spectrometry of compounds with two or more adjacent quaternary centres is interesting because of two opposite trends: the facile fragmentation of the C^{quart}—C^{quart} bond(s) on the one hand, and the possibility of rearrangement processes due to the proximity of substituents at the quaternary atoms on the other. We report here on a particular interesting case, ionized 1,1,2,2,3,3-hexamethylidan ([2]$^{+\cdot}$) and, in particular, on the isomerization and fragmentation reactions of the ions generated by loss of a methyl group, [2 − CH$_3$]$^+$.[1]

In the course of our studies on centropolyindans,[2] we studied the synthesis of 1,1,3,3-tetramethylated indans with two additional substituents at C(2) from the corresponding disubstituted indan-1,3-diones by using Reetz's reagent, dimethyltitanium dichloride, (CH$_3$)$_2$TiCl$_2$.[3] The only successful reaction found was the formation of the title compound, 2, obtained in 40% isolated yield from 2,2-dimethylindan-1,3-dione (1) (Scheme 1, path a). The 70 eV electron impact (EI) mass spectrum of 2 (Fig. 1) showed a peak at m/z 57 of considerable (∼40% B) intensity, that is, the formation of C$_4$H$_9$$^+$ ions, indicating extensive rearrangement processes in the course of the fragmentation.

From an analytical point of view, the observation of C$_4$H$_9$$^+$ ions in the mass spectrum of 2 is particularly
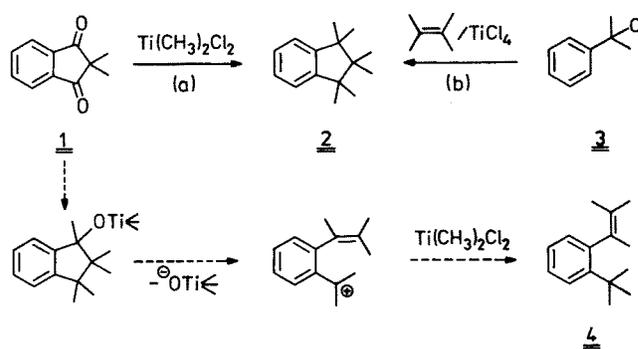
Scheme 1

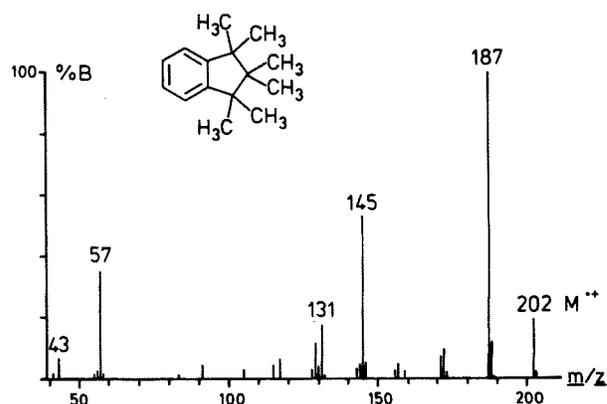Figure 1. EI mass spectrum (70 eV) of 1,1,2,2,3,3-hexamethylindan (2).

intriguing because of the potential formation of isomers which do bear a (tertiary) butyl group, e.g. 4, as a by-product of the methylation reaction (the m/z 57 peak is present with $\sim 25\%$ B intensity in the mass spectra of several isomers of 2, viz. 1,1-dimethylindans bearing a tert- or n-butyl substituent at the benzo ring[4]). Although independent analysis of 2 by ^{1}H NMR and gas chromatography/mass spectrometry did not indicate any impurities of type 4, its formation appeared possible on mechanistic grounds, as shown in Scheme 1. Owing to the preformed tert-butyl group, expulsion of $C_4H_9{}^+$ could be anticipated to occur readily from ions [4][+.], in contrast to ions [2][+.], by intramolecular hydrogen rearrangement.[4] During our work, Baran and Mayr[5] published an independent synthesis of 2 (Scheme 1, path b), which inherently excluded the formation of 4-type isomers, but the mass spectrum of Baran and Mayr's product proved to be identical with that of our hydrocarbon.[6]

In this paper, we present the results of an isotope-labelling study which was performed in order to establish the fragmentation of the title compound 2 under EI conditions. It will be shown that the salient features of the fragmentation can be unravelled by analysing the intriguing formation of $C_4H_9{}^+$. This then allows one to deduce also the competing breakdown paths to two other characteristic peaks in the mass spectrum of 2, i.e. those of ions $C_{10}H_{11}^+$ (m/z 131) and $C_{11}H_{13}^+$ (m/z 145).

## RESULTS AND DISCUSSION

Origin of the $C_4H_9{}^+$ ions

The mass-analysed ion kinetic energy (MIKE) spectrum[7,8] of ions [2][+.] shows only one signal, viz. loss of $CH_3{}^{\cdot}$. Hence the $C_4H_9{}^+$ ions observed in the normal 70 eV mass spectrum are certainly not primary fragmentation products. The MIKE spectra of the deuterium-labelled analogous 2a–d (Table 1) clearly document that the methyl groups at the benzylic posi-

Table 1. Methyl loss from metastable 1,1,2,2,3,3-hexamethylindan radical cations [2][+.]–[2d][+.] (MIKE spectra)[a]

Compound	Label	[M − CH₃]⁺	[M − CD₃]⁺
2	D_0	100	0
2a	Benzo-D_4	100	0
2b	1,1-$(CD_3)_2$	63.3	36.7
2c	2,2-$(CD_3)_2$	94.5	5.5
2d	2-CD_3	97.7	2.3

[a] In % Σ; error limit $\pm 1\%$.

tions [C(1) and C(3)] are lost much more readily than those at the homobenzylic position [C(2)], as expected on the basis of localized bond activation. The quantitative approach reveals that 92% of the metastable ions lose $CH_3{}^{\cdot}$ from C(1) and C(3) and only 8% from C(2). A quantitative evaluation assuming two distinct isotope effects suffers from the experimental error on the large ion abundance ratios [M − CH_3]⁺/[M − CD_3]⁺ for 2c and, in particular, 2d; therefore, an averaged kinetic isotope effect i_1 was evaluated from the data for 2b and 2c. This secondary kinetic isotope effect is relatively large ($i_1 = 1.47$) and corresponds to the kinetic isotope effect in long-lived, metastable tert-butylbenzene radical cations ($1.8 \leqslant i \leqslant 1.9$) has been reported[9]. The six methyl groups do not interchange their positions, nor do they scramble hydrogen atoms with other portions
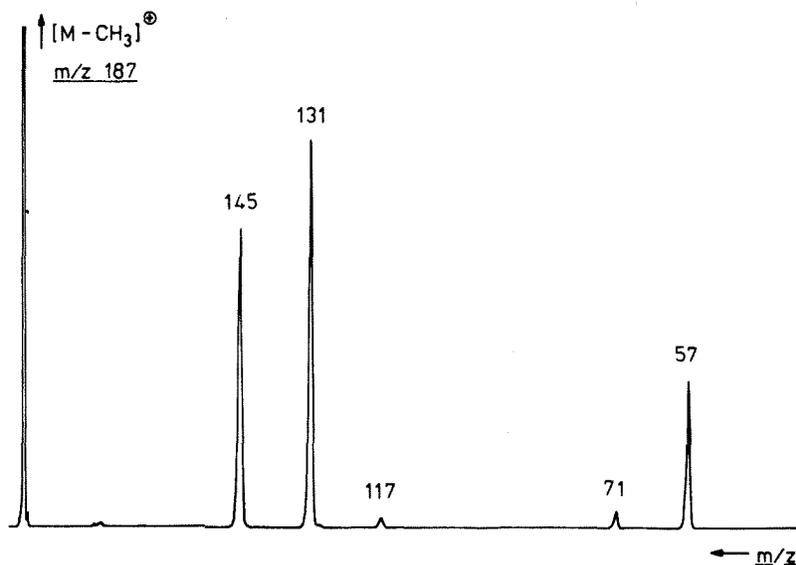
Figure 2. MIKE spectrum of [M − CH₃]⁺ ions of 2 (m/z 187).

of the molecular ion prior to the primary fragmentation. Obviously, the primary fragmentation of ions [2]$^{+\cdot}$ corresponds to the similarly straightforward methyl loss from radical cations of tert-butylbenzene.[9]

The MIKE spectrum of ions [2 − CH$_3$]$^+$ (Fig. 2) reveals three major fragmentations: (i) formation of ions C$_4$H$_9^+$ (m/z 57), (ii) loss of C$_4$H$_8$ leading to ions C$_{10}$H$_{11}^+$ (m/z 131) and (iii) loss of C$_3$H$_6$, to give ions C$_{11}$H$_{13}^+$ (m/z 145). Processes (i) and (ii) represent, at least formally, complementary reaction channels in that a proton continues at either a C$_4$H$_8$ or a C$_{10}$H$_{10}$ neutral fragment. The conjugate to process (iii), i.e. formation of C$_3$H$_7^+$ ions, does not occur in the metastable [2 − CH$_3$]$^+$ ions but gives rise to a minor peak in the 70 eV standard spectrum (Fig. 1). Minor fragmentation paths of the metastable ions are formation of C$_5$H$_{11}^+$ (m/z 71) and the complementary loss of C$_5$H$_{10}$ to give ions C$_9$H$_9^+$ (m/z 117). The fact that the three major paths prevail in both the low and high internal energy regimes suggests that the m/z 57 peak in the standard 70 eV spectrum of 2 is completely due to a rearrangement process occurring on the level of the primary fragment ions [2 − H]$^+$ (m/z 187).

Methyl group equilibration in the [M − methyl]$^+$ ions and the structure of C$_4$H$_9^+$

The MIKE spectra of the [M − methyl]$^+$ ions formed from the labelled hexamethylindans 2a–d are given in Tables 2–4. The spectrum of ions [2a − CH$_3$]$^+$ shows that the hydrogen atoms at the benzo nucleus are completely or almost completely retained during all of the major fragmentation processes. Hence, no skeletal isomerization of the aromatic moiety, well known from other C$_7$H$_7^+$-type ions,[1a] occurs in the [M − CH$_3$]$^+$ ions. By contrast, the isomerization of the [M − methyl]$^+$ ions is evident from the three isotopomers 2b–d.

Table 2. Formation of tert-butyl ions[a] from metastable [M − methyl]$^+$ ions of 1,1,2,2,3,3-hexamethylindan 2–2d (MIKE spectra)[b]

Precursor compound	Ion	m/z	C$_4$H$_9^+$ 57[c]	C$_4$H$_6$D$_3^+$ 60[c]	C$_4$H$_3$D$_6^+$ 63[c]
2	[M − CH$_3$]$^+$	187	100	—	—
2a	[M − CH$_3$]$^+$	191	100	0	—
2b	[M − CH$_3$]$^+$	193	6.2	55.1	38.7
2c	[M − CH$_3$]$^+$	193	6.1	55.8	38.1
2b	[M − CD$_3$]$^+$	190	34.1	65.9	—
2c	[M − CD$_3$]$^+$	190	32.9	67.1	—
2d	[M − CH$_3$]$^+$	190	32.7	67.3	—
Calculated for methyl group equilibrium					
$i_2 = 1.0$[d]		193	10.0	60.0	30.0
$i_2 = 1.0$[d]		190	40.0	60.0	
$i_2 = 2.0$[d]		193	6.3	56.2	37.2
$i_2 = 2.0$[d]		190	33.3	66.7	

[a] For the tertiary structure of C$_4$H$_9^+$, see text.
[b] In % Σ, error limits ±2%.
[c] No ion abundances at intermediate masses (m/z 58, etc.) observed.
[d] Kinetic isotope effect i_2 assumed to be rate limiting in the step c → d (Scheme 3). Alternatively, an equilibrium isotope effect can operate (see text).

Of the three major elimination reactions, process (i) gives a particularly clear picture and will be analysed first. Surprisingly, the MIKE spectra of the various D$_3$- and D$_6$-labelled [M − methyl]$^+$ ions (Table 2) are identical within the limits of experimental error, and only C$_4$(H,D)$_9^+$ ions with D$_0$, D$_3$ and D$_6$ isotope contents are formed (Fig. 3). The relative abundances of the three isotopomers are close to the pattern calculated for statistical interchange of the five methyl groups prior to fragmentation, and an isotope effect operates in favour of the heavier C$_4$(H,D)$_9^+$ isotopomers (Table 2). Hence the five methyl groups in the [M − CH$_3$]$^+$ ions are completely equilibrated, apparently without any disintegration of C—H bonds. As will be shown below, the same conclusion can be drawn from the relative ion abundances corresponding to the loss of C$_4$(H,D)$_8$ from the labelled [M − methyl]$^+$ precursors.

As shown in Scheme 2, the methyl group equilibration takes place by multiple 1,2-shifts at the five-membered ring, probably without involving the aromatic nucleus. In this way, the pentamethylated 1- and 2-indanyl ions a and b, which originate from the site-specific methyl loss from [2]$^{+\cdot}$, are equilibrated prior to further skeletal rearrangement and secondary fragmentation. In a recent NMR study on the fast circumambulatory migration of methyl groups in nonamethylcyclopentyl ions, Mayr and Koschinsk[10] deduced remarkably low energy barriers ($\Delta G^{\ddagger} = 29.3$ kJ mol^{-1}) in superacid solutions at −120 °C. From the notably good agreement between solution and recent experimental and computational gas-phase activation barriers on the proton shift in alkylbenzenium ions,[1b,11,12] it may be assumed that the activation barrier of the methyl shift $a \rightleftharpoons b$ in gaseous [2 − CH$_3$]$^+$ ions may be close to the value mentioned above. In the gaseous closed-shell carbenium ions, shifts of intact methyl groups are not frequently encountered, but they may play a more important role than usually considered.[13]

The fact that the methyl groups constituting the C$_4$H$_9^+$ ions remain intact during the isomerization process suggests that these fragment ions have the tert-butyl structure, at least when formed from the low-energy, metastable ions (Scheme 2).

The isotope effect operating in favour of the formation of the heavier tert-butyl ions might be interpreted as a hint to a 'hidden' hydrogen transfer[14] occurring in the rate-limiting step of the fragmentation. In fact, a hidden proton transfer step is necessary to initiate the formation of a tert-butyl grouping (see below), and a primary kinetic isotope effect ($i_2 = 2.0$) assumed for this step allows a perfect simulation of the experimental data (Table 2). Alternatively, however, the deviations from the statistical patterns may be due to a thermodynamic isotope effect (see below).

Mechanism of t-C$_4$H$_9^+$ ion formation and isotope effects

The mechanistic rationalization of the results presented so far is outlined in Scheme 3. The equilibrium between the indanyl ions a and b is intercepted by heterolytic cleavage of the five-membered ring, a process corresponding to the Grob fragmentation[15] known to occur,
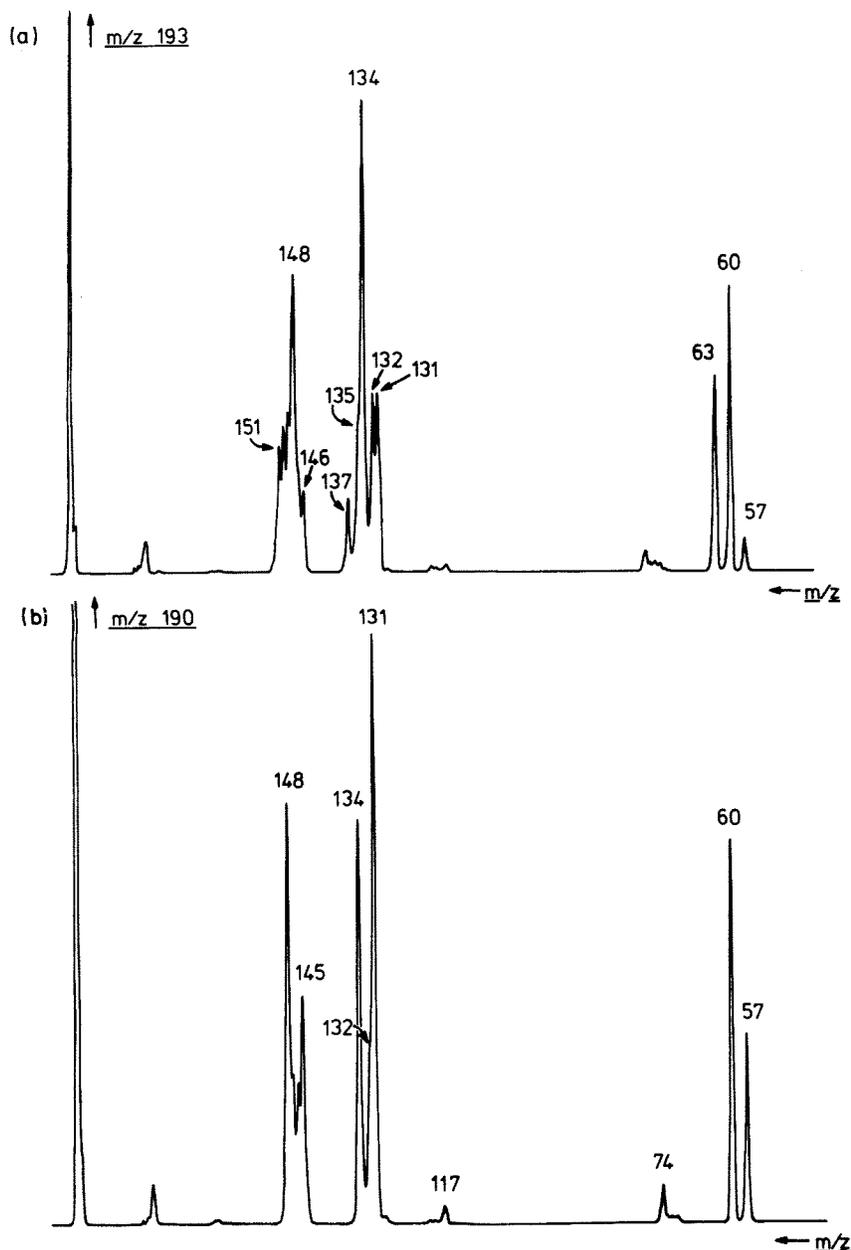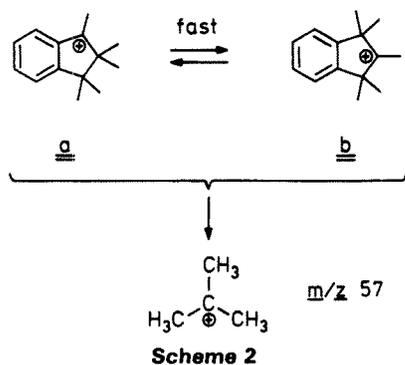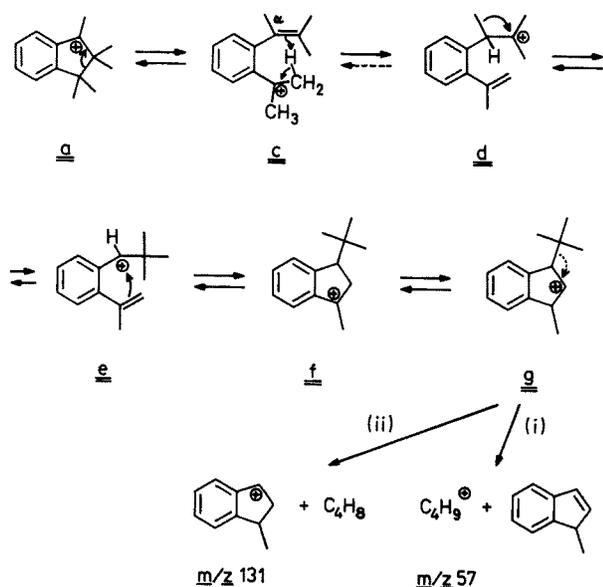
Figure 3. MIKE spectra of (a) [M – CH₃]⁺ ions (m/z 193) and of (b) [M – CD₃]⁺ ions (m/z 190) of **2b**.

inter alia, with indan-1,3-diols in acidic solution.[16] Subsequent isomerization of ion *c* by proton transfer from one of the 'acidified' methyl groups of the isopropylidene moiety to the α-position of the newly formed

Scheme 2

double bond gives rise to ion *d*. This step involves the only disintegration of a methyl group *en route* to the t-$C_4H_9^+$ ions, and it may be noted that it could well be reversible ($c \rightleftharpoons d$) without effecting hydrogen exchange, in accordance with the experimental findings. As will be shown in the following sections, the conversion $c \rightarrow d$ leads also to the formation of complementary fragment ions, viz. $C_{10}H_{11}^+$, whereas the competing proton transfer to the β-position ($c \rightarrow h$, Scheme 5) gives rise to the formation of $C_{11}H_{13}^+$ ions. Next, the formation of the *tert*-butyl sub-structure requires a 1,2-methyl shift to give ion *e*, which subsequently isomerizes to (*tert*-butyl) methylindanyl ions *f* and *g* by ring closure and 1,2-hydride shift. Ion *g* is suggested to be the species from which, eventually, the *tert*-butyl ion is extricated.

The intermediate ions *f* and *g*, being 1- and 2-indanyl ions as are ions *a* and *b*, could also equilibrate. However, the stability difference of unsubstituted 1- and

Scheme 3

sequence $a \rightarrow g$ to be subject to a *thermodynamic* isotope effect. It is well known from solution chemistry[18] that carbenium ions bearing CD_3 groups α to the centre of formal charge are destabilized relative to those bearing CH_3 groups at that position. Assuming, in the case under consideration, a reversible equilibrium $a \rightleftharpoons g$ as shown in Scheme 3, a good candidate for this 'isotopic perturbation of degeneracy'[19] in favour of the isotopomer with the heavier *tert*-butyl groups is ion f, as outlined in Scheme 4(b).

Formation of $C_{10}H_{11}^+$ ions—the same mechanism as mirrored in the conjugate fragmentation channel

Although less evident, the loss of labelled butenes from the [M − methyl]$^+$ ions to give ions $C_{10}(H,D)_{11}^+$ (Fig. 3, Table 3) is in full agreement with the details of the isomerization mechanism proposed for the formation of t-$C_4(H,D)_9^+$ ions. Even the kinetic (or equilibrium) isotope effect deduced for the latter process is reflected in the relative abundances of the $C_{10}(H,D)_{11}^+$ ions. First, the fragmentation of the various D_3- and D_6-labelled [M − methyl]$^+$ ions is again identical. Further, however, it is particularly enlightening that the two sets of relative abundances of the [M − methyl − $C_4(H,D)_8$]$^+$ ions (m/z 131–134 and 131–137, respectively) almost perfectly mirror those of the corresponding t-$C_4H_9^+$ ions. This is illustrated in Fig. 4 for the case of the D_6-labelled [M − methyl]$^+$ ions (m/z 193). As a consequence of this mirror-like behaviour, the neutral species lost is assigned the structure of isobutenes.

Ions $C_{10}H_5D_6^+$ (m/z 193) expel essentially five isobutene isotopomers (Fig. 4), which can be divided into three subgroups, viz. the D_6 and D_5, the D_3 and D_2, and the D_0 isotopomers. The (averaged) abundance ratios [(m/z 131) + (m/z 132)] : [(m/z 134) + (m/z 135)] : (m/z 137) = 33.2 : 56.1 : 6.9 are strikingly close to those

2-indanyl ions is relatively large ($\Delta\Delta H_f \approx 75$ kJ mol^{-1});[17] thus the critical energy for the hydride transfer ($f \rightarrow g$) may exceed that of the methyl shift ($a \rightarrow b$). As a consequence, both the proton transfer ($c \rightarrow d$) and the hydride shift ($f \rightarrow g$) may represent the rate-determining step of the isomerization, and a kinetic isotope effect (i_2, Table 2), operating in favour of the formation of the heavier $C_4(H,D)_9^+$ ions, may be traced to either of these steps. Only the first of these two possibilities is illustrated in Scheme 4(a).
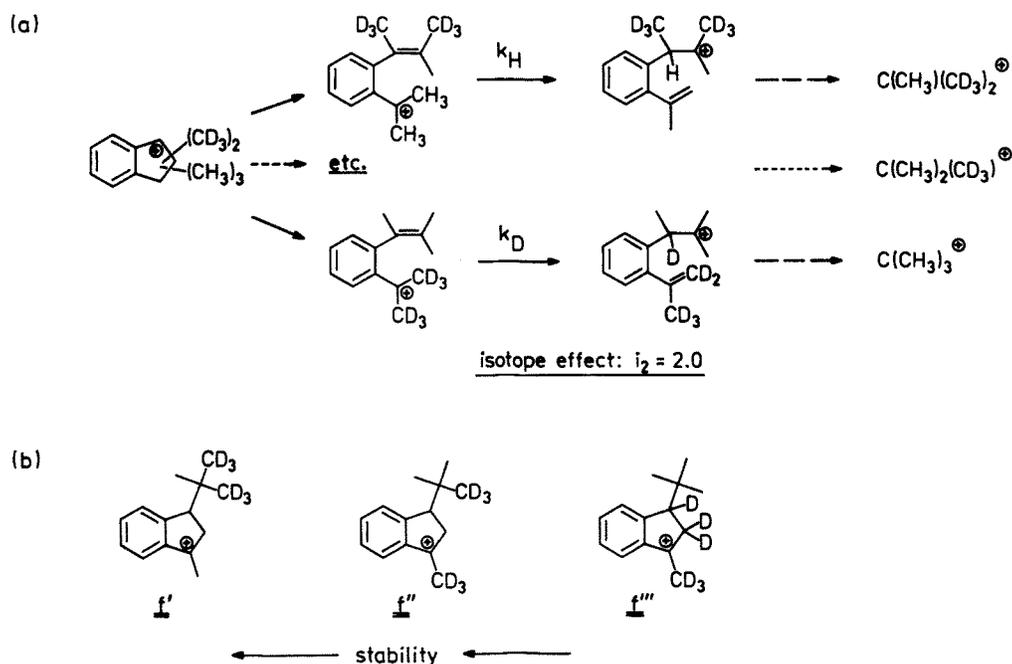
This explanation would be satisfactory were it not for the finding that the process conjugate to the formation of t-$C_4H_9^+$, i.e. elimination of C_4H_8, exhibits *two* isotope effects, one of them certainly being kinetic. Therefore, we suspect the skeletal isomerization

isotope effect: $i_2 = 2.0$

stability

Scheme 4

Table 3. Loss of isobutene from metastable [M − methyl]⁺ ions of 1,1,2,2,3,3-hexamethylidan 2–2d (MIKE spectra)[b]

Precursor compound	Ion	m/z	$C_{10}H_{11}^+$ 131	$C_{11}H_{10}D^+$ 132	$C_{11}H_9D_2^+$ 133	$C_{11}H_8D_3^+$ 134	$C_{11}H_7D_4^+$ 135	$C_{11}H_6D_5^+$ 136	$C_{11}H_5D_6^+$ 137
2	[M − CH₃]⁺	187	100	—	—	—	—	—	—
2a	[M − CH₃]⁺	191	0	0	0	0	100	—	—
2b	[M − CH₃]⁺	193	16.4	16.2	2.6	44.9	11.1	1.8	7.1
2c	[M − CH₃]⁺	193	17.2	16.6	2.5	44.9	11.2	1.1	6.7
2b	[M − CD₃]⁺	190	50.9	12.8	1.6	34.7	—	—	—
2c	[M − CD₃]⁺	190	50.2	13.7	1.4	34.8	—	—	—
2d	[M − CH₃]⁺	190	51.0	12.9	1.4	34.7	—	—	—

[a] For the structure of C_4H_8, see text.
[b] In % Σ, error limits ±3%.

found for the corresponding *tert*-butyl ions (Table 2), that is, $(m/z\ 63):(m/z\ 60):(m/z\ 57) = 38.4:55.5:6.2$. The slight discrepancy between the two sets of ratios appears to be due to the elimination of small amounts of D₄- and D₂-isobutenes giving rise to ions with m/z 133 and 136, the contributions of which have been excluded. Correspondingly, the precursor ions $C_{10}H_8D_3^+$ (m/z 190) eliminate mainly three isobutene isotopomers in two subgroups, viz. $C_4H_5D_3$ and $C_4H_6D_2$ as well as C_4H_8, with the averaged abundance ratio $[(m/z\ 131) + (m/z\ 132)]:(m/z\ 134) = 63.8:35.2$ being again very close to that for the corresponding *tert*-butyl ions, $(m/z\ 60):(m/z\ 57) = 66.8:33.2$.

Clearly, this mirror-like behaviour suggests that both ions $C_4H_9^+$ and $C_{10}H_{11}^+$ are formed via the same intermediates (Scheme 3), the last of which, ion g, expels either $C_4H_9^+$ or, after hydrogen rearrangement, isobutene to give $C_{10}H_{11}^+$ ions. In the case of the D₆-labelled analogues, for example, three sets of isotopomers $[f'/g',\ f''/g''$ and $f'''/g''';$ cf. Scheme 4(b) for ions $f]$ are formed with the relative abundances given above. In competition with the direct cleavage to give the labelled *tert*-butyl ions, ions g' and g'' each expel the corresponding pair of isobutenes by rearrangement of either a proton or a deuteron, whereas the minor fraction, ions g''', eliminate only C_4H_8. Hence, after statistical correction, the observed ion abundance ratios $(m/z\ 131):(m/z\ 132) = 1.0$ and $(m/z\ 134):(m/z\ 135) = 4.0$ for ions $C_{10}H_5D_6^+$ (m/z 193, Table 3) both yield a

kinetic isotope effect $i_3 = k_H:k_D = 2.0\ (\pm 0.1)$. Accordingly, the D₃-labelled [M − methyl]⁺ ions (m/z 190, Table 3) lose $C_4H_5D_3$ and $C_4H_6D_2$ in the ratio (m/z 131):(m/z 132) = 4.0, leading to $i_3 = 2.0\ (\pm 0.1)$ as well.

### Formation of $C_{11}H_{13}^+$ ions—another but less clear mirror

Loss of propene from [M − CH₃]⁺ ions (process iii) generates the fragment ions $C_{11}H_{13}^+$. In spite of the lack of direct evidence for the persistence of intact methyl groups prior to the expulsion of C_3H_6, indirect information is obtained by analysis of the $C_{11}(H,D)_{13}^+$ ion abundance patterns (Table 4). They can be rationalized by a mechanism similar to that proposed for the loss of isobutene. Loss of propene is induced by proton (or deuteron) transfer from the isopropylidene group to the β-position of the double bond to give ion h (Scheme 5). Alternatively, ion h could be formed by 1,2-hydride shift from d, instead of the 1,2-methyl shift ($d \rightarrow e$, Scheme 3). Ring closure of ion h followed by 1,2-hydride shift gives rise to the formation of 1-isopropyl-1,3-dimethylindanyl ions i and j, from which C_3H_6 may be eliminated. Again, this mechanism excludes hydrogen exchange between the methyl groups throughout the isomerization process $a \rightarrow j$, as will be corroborated by a quantitative evaluation of the experimental data.

Several factors may influence the relative abundances of the $C_{11}(H,D)_{13}^+$ ions. In this case, hydrogen exchange between the alicyclic and the aromatic moieties occurs to a small extent, as indicated by ~5% of ions with m/z
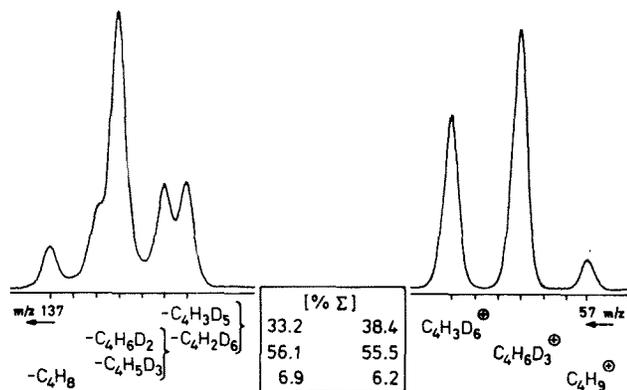
Figure 4. Comparison of the peak clusters for loss of isobutenes (left) and for formation of *tert*-butyl ions (right) from the [M − CH₃]⁺ ions of **2b**.
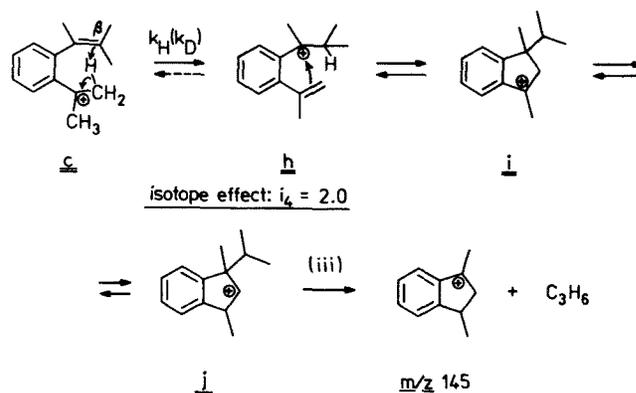
Scheme 5

Table 4. Loss of propene from metastable [M − methyl]⁺ ions of 1,1,2,2,3,3-hexamethylindan 2–2d (MIKE spectra)[a]

Precursor compound	Ion	m/z	$C_{11}H_{13}^+$ 145	$C_{11}H_{12}D^+$ 146	$C_{11}H_{11}D_2^+$ 147	$C_{11}H_{10}D_3^+$ 148	$C_{11}H_9D_4^+$ 149	$C_{11}H_8D_5^+$ 150	$C_{11}H_7D_6^+$ 151
2	$[M-CH_3]^+$	187	100	—	—	—	—	—	—
2a	$[M-CH_3]^+$	191	0	0	0	4.9	95.1	—	—
2b	$[M-CH_3]^+$	193	0	9.9	7.5	35.8	16.0	15.4	15.5
2c	$[M-CH_3]^+$	193	0	9.1	8.5	35.9	16.5	15.2	14.9
2b	$[M-CD_3]^+$	190	25.3	13.4	12.5	48.8	—	—	—
2c	$[M-CD_3]^+$	190	25.7	14.2	12.8	47.3	—	—	—
2d	$[M-CH_3]^+$	190	26.1	13.7	12.6	47.6	—	—	—

Calculated for equilibrium of three CH_3 and two CD_3 groups *and additional* H/D randomization within the isopropyl group[b]

A	$(i_4 \equiv i_5 \equiv 1.0)^c$	193	1.4	8.6	8.6	34.3	17.1	17.1	12.8
B	$(i_4 \equiv i_5 \equiv 1.5)^c$	193	1.9	7.6	7.6	37.3	15.3	15.3	15.0
C	$(i_4 \equiv i_5 \equiv 2.0)^c$	193	2.2	6.7	6.7	40.4	13.5	13.5	16.9
D	$(i_4 \equiv i_5 \equiv 2.0)^c$	193	2.2	6.7	6.7	40.4	13.5	13.5	16.9

Calculated for equilibrium of three CH_3 and two CD_3 groups but *excluding* H/D randomization within the isopropyl group[b]

E	$(i_4 \equiv i_5 \equiv 1.0)^c$	193	—	10.0	10.0	30.0	20.0	20.0	10.0
F	$(i_4 \equiv i_5 \equiv 1.5)^c$	193	—	9.0	9.0	32.8	17.9	17.9	13.4
G	$(i_4 \equiv i_5 \equiv 2.0)^c$	193	—	8.0	8.0	36.0	16.0	16.0	16.0
H	$(i_4 \equiv 2.0, i_5 \equiv 1.5)^c$	193	—	9.8	7.3	34.1	19.5	14.6	14.6
I	$(i_4 \equiv 2.0, i_5 \equiv 1.85)^c$	193	—	8.5	7.8	35.5	16.9	15.6	15.6

[a] In % Σ, error limits ±3%.
[b] Calculated for the rearrangement shown in Scheme 4.
[c] Isotope effects of the H⁺ or D⁺ transfer steps.

148 in the MIKE spectrum of the benzo-D_4-labelled precursor ions $[2a - CH_3]^+$ (Table 4). Further, because of the formal similarity of propene and isobutene elimination reactions, again *two* isotope effects may be expected: first, a kinetic effect (i_4, Scheme 5), affecting the proton transfer step $c \rightarrow h$ or the hydride shift $i \rightarrow j$ (or, alternatively, a thermodynamic effect affecting the equilibrium of the various isotopomers involved), and second, another kinetic isotope effect (i_5) operating during the final elimination step. Lastly, in contrast to the elimination of isobutene, the possibility of hydrogen exchange within the incipient isopropyl group has to be considered.

Extensive model calculations have been performed to simulate the abundance pattern of the $C_{11}(H,D)_{13}^+$ ions. Some of the results are included in Table 4. Two sets of quantitative model calculations with different combinations of isotope effects (k_4 and k_5) have been performed. The first assumes randomization of the seven hydrogen atoms of the isopropyl group prior to propene loss and predicts, for the D_6-labelled precursor ions (Table 4, entries A–D), minor but significant contributions of *unlabelled* $C_{11}H_{13}^+$ ions (m/z 145). In contrast, by assuming specific hydrogen transfer from the CH_3 and CD_3 methyl groups of the incipient isopropyl grouping, i.e. without participation of the H or D atoms from the tertiary position, ions $C_{11}H_{13}^+$ cannot be formed at all (Table 4, entries E–I). In fact, the experimental pattern of the D_6-labelled $[M - methyl]^+$ do not exhibit a component at m/z 145, suggesting specific hydrogen rearrangmeent without scrambling.

Within the latter model, the best fit of the simulated $C_{11}(H,D)_{13}^+$ ion abundances to the experimental pattern is obtained with $i_4 = 2.0 \pm 0.1$ and $i_5 = 1.85 \pm 0.15$ (Table 4, entry I). It is striking that i_4, which is considered here a kinetic isotope effect operating within the

skeletal isomerization sequence $a \rightarrow j$, is identical with the kinetic isotope effect ($i_2 = 2.0$) calculated for the corresponding competing sequence $a \rightarrow g$. In turn, this may represent another hint to the alternative possibility that both isomerization sequences are subject to the same thermodynamic isotope effect, effecting, for example, the equilibrium $a \rightleftharpoons c$ (Scheme 3) common to both isomerization pathways. The primary isotope effect i_5, operating on the final elimination of propene, appears to be slightly smaller than that of the competing loss of isobutene ($i_3 = 2.0$).

Ion–molecule complexes as possible intermediates during the fragmentation of the [M − methyl]⁺ ions

All three elimination processes (i–iii) analysed in the previous sections could be elegantly explained by assuming ion–neutral complexes as the final intermediates. Thus, complex $[C_4H_9^+ \cdot C_{10}H_{10}]$ (k, Scheme 6) may be formed prior to expulsion of the t-$C_4H_9^+$ ions and to the elimination of isobutene. The related complex $[C_3H_7^+ \cdot C_{11}H_{12}]$ (l, Scheme 6) may be the species from which the propene neutral is eventually expelled. This view appears particularly attractive because of the perfect mirror-like behaviour of the $[M - CH_3]^+$ ions, as far as the processes (i) and (ii) are concerned, and because of the possibility that a common thermodynamic isotope effect may operate on the skeletal isomerization which precedes both loss of isobutene and propene (processes ii and iii). Methyl- and dimethylindenes appear to be the best candidates as the neutral component in these complexes.

The proton affinities (PA) of methylindenes are not known, but they should exceed that reported for indene ($PA = 854$ kJ mol⁻¹).[17] The comparison with

Scheme 6
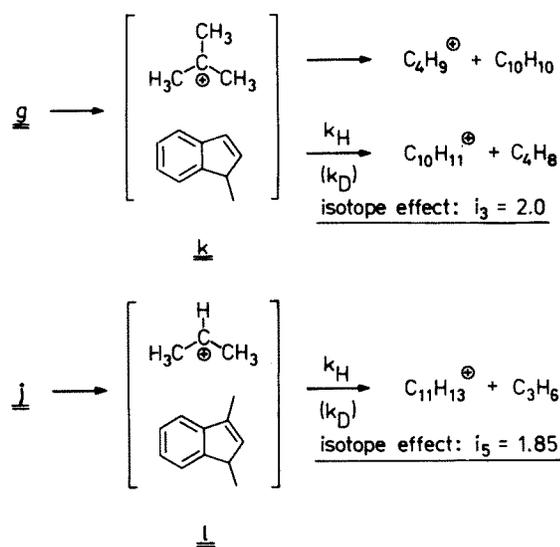
$PA(i\text{-}C_4H_8) = 808$ kJ mol^{-1} (Ref. 20) shows that the loss of isobutene from $[M - CH_3]^+$ should be more favourable by >46 kJ mol^{-1} than the formation of $C_4H_9^+$. On the other hand, the observed competition of the three processes (i)–(iii) suggests that the corresponding critical energies are similar and that, consequently, the elimination of isobutene (and probably also that of propene) are associated with reverse activation energies. The kinetic energy releases for processes (i) and (ii) are closely similar, $T_{(i)} = 20.8$ meV and $T_{(ii)} = 21.7$ meV, whereas $T_{(iii)} = 26.0$ meV (measured at half-height). In line with that, no significant hydrogen exchange is observed during the latter two processes. The lack of the complementary elimination reaction, i.e. formation of $C_3H_7^+$ ions, is attributed to the even larger PA difference of the corresponding olefins: $PA(C_{11}H_{12}) - PA(C_3H_6) > 96$ kJ mol^{-1}.[17,20] A schematic energy profile for this situation is given in Fig. 5.

Other arguments may disfavour the formation of complexes k and l. As shown in recent studies by Audier et al.[21] and by ourselves,[22] tert-butyl-substituted alkylbenzenium ions ($t\text{-}C_4H_9C_6H_5^+$—R, with R $\geqslant C_2H_5$) expel isobutane instead of (or together with) isobutene

and/or tert-butyl cations. The intermediacy of unimolecularly generated ion–molecule complexes is obvious in those species, and isobutane loss represents the most energetically favourable fragmentation path. Hence the formation of complex k might also be indicated by loss of isobutane. However, a thermochemical estimation using the currently available data casts doubts on whether the loss of isobutane from complex k is more exothermic than the simple separation of the components. [With $\Delta H_f(\text{indenyl}^+) = 1000$ kJ mol^{-1},[23] the hydride abstraction reaction from indene, i.e. $C_9H_8 + t\text{-}C_4H_9^+ \rightarrow C_9H_7^+ + i\text{-}C_4H_{10}$, is endothermic by $\sim +8.4$ kJ mol^{-1} (other data taken from Ref. 20). However, the experimental values of $\Delta H_f(\text{indenyl}^+)$ measured by the semi-logarithmic plot technique has been a matter of much debate[20,24] and higher values must also be considered.[23] Hence it seems questionable whether the reaction may become slightly exothermic with methyl-substituted indenes (cf. k and l). The only reported value of $\Delta H_f(1\text{-methylindenyl}^+) = 954$ kJ mol^{-1} (Ref. 25b) also suggests an endothermic hydride transfer.][23–25]

The isopropyl cation present in complex l may be assumed to undergo fast randomization of its seven hydrogen atoms, in contrast to the experimental findings discussed in the previous section. However, a recent study by Audier and co-workers[26] also demonstrates that the H(2) atom of the ionic partner in the ion–neutral complex $[CH^+(CH_3)_2 \quad C_6H_6]$ formed during the fragmentation of isopropylbenzium ions is not involved in hydrogen exchange. Therefore, the site specificity found for loss of propene from $[M - CH_3]^+$ does not rule out the intermediacy of complex l.

CONCLUSION

The EI-induced fragmentation of 1,1,2,2,3,3-hexamethylindan (**2**) has been investigated in detail. The intriguing formation of tert-butyl ions and the elimination of isobutene and propene occurs via the $[M - CH_3]^+$ ions. Methyl group equilibration within these ions is complete prior to a series of skeletal and
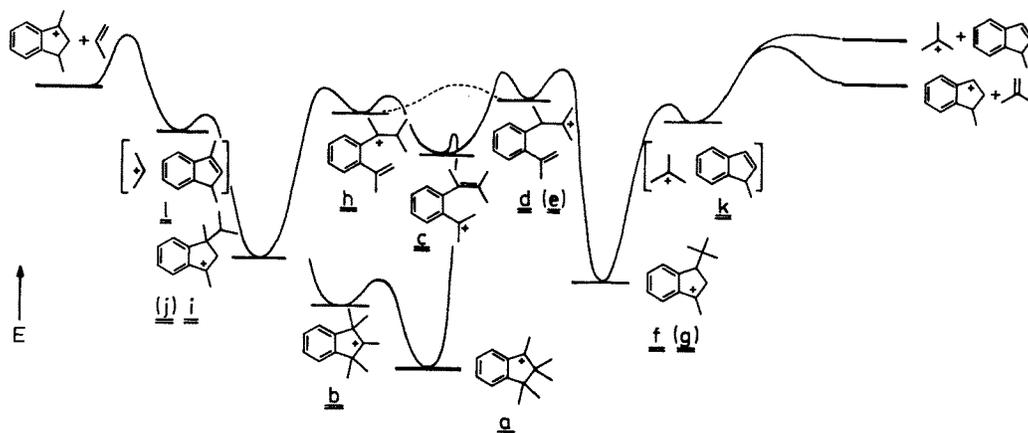
Figure 5. Schematic energy profile for isomerization and fragmentation of the $[M - CH_3]^+$ ions of **2**. Intermediates e, g and j (Schemes 3 and 5, respectively) have been omitted. The energy scale is qualitative (see text).

hydrogen rearrangements leading to the formation of tert-butyl- and sec-propyl-substituted methylindanyl ions, from which t-$C_4H_9^+$ as well as i-C_4H_8 and C_3H_6 are expelled. The interplay of several isotope effects and the suggested intermediacy of ion–neutral complexes indicate that highly methylated benzocycloalkanes of type 2 may undergo complex, but mechanistically reasonable, isomerization processes as the origin of unexpected and analytically intriguing fragmentation behaviour.

EXPERIMENTAL

The standard mass spectra were measured with a Finnigan MAT CH5-DF instrument (electron energy 70 eV, emission current 100 µA, accelerating voltage 4 kV, source temperature 180 °C). The ^1H NMR spectra were obtained with a Bruker WP80 instrument. The MIKE spectrometric measurements were performed with a VG Analytical ZAB-2F mass spectrometer (70 eV, trap current 100 µA, 6 kV, ~200 °C). The samples were introduced with a heated inlet system assembled in this laboratory.

2,2-Dimethylindan-1,3-dione (1) and 2,2-bis(trideuteromethyl)indan-1,3-dione (1c)

These were prepared according to Bloch and Orvane[27] by reaction of indan-1,3-dione and methyl iodide or [D_3]methyl iodide, respectively, with potassium fluoride on Celite 545 (Fluka) in acetonitrile.

2-Methyl-2-(trideuteromethyl)indan-1,3-dione (1d)

This was prepared in a similar manner from 2-methylindan-1,3-dione[28] and [D_3]methyl iodide.

1,1,2,2,3,3-Hexamethylindan (2)

Compound 2 was synthesized by methylation of 1 with $Ti(CH_3)_2Cl_2$. A solution of titanium tetrachloride (10.8 mmol) in 19.6 cm³ of dry dichloromethane was stirred at -30 °C in the predried two-necked bulb under nitrogen, and a solution of dimethylzinc[29] (10.8 mmol) in the same solvent was injected through a rubber septum. The mixture was stirred for 30 min at this temperature to allow formation of 2, and a concentrated solution of 1 (0.39 g, 2.25 mmol) in dichloromethane was added slowly without raising the temperature. The reaction mixture was allowed to warm to room temperature, while stirring was continued, and then poured into ice–water. After extraction with dichloromethane, the extract was washed with water and aqueous sodium hydrogencarbonate solution and dried with magnesium sulphate. After removal of the solvent the residue was distilled in a Kugelrohr apparatus to give a colourless oil, b.p. 138 °C/18 mbar (1 bar = 10^5 Pa), in 40% yield.

^1H NMR (80 MHz, $CDCl_3$), δ (ppm) 0.88 (6H), 1.20 (12H), 7.15 (4H). The IR and 70 eV mass spectra (see Fig. 1) agreed with the data given by Baran and Mayr.[5,6]

4,5,6,7-Tetradeutero-1,1,2,2,3,3-hexamethylindan (2a)

According to standard procedures for the unlabelled compounds, [D_5]phenylmagnesium bromide was reacted with acetone to give 2-([D_5]phenyl)propan-2-ol (92%), and the alcohol was converted to 2-chloro-2-([D_5]phenyl)propane (57%) by using gaseous hydrogen chloride. No significant loss of label was observed. In analogy with the procedure of Baran and Mayr[5] for unlabelled 2, a solution of the D_5-labelled chloride (2.1 g, 13 mmol) and of 2,3-dimethylbut-2-ene in 40 cm³ of dichloromethane (freshly distilled from P_4O_{10}) was stirred and cooled to -75 °C under nitrogen, and titanium tetrachloride (0.25 cm³) was added during 10 min through a rubber septum. After stirring for 1 h, the mixture was poured into 10% HCl. After extraction with dichloromethane, drying of the extract with $MgSO_4$ and removal of the solvent, 2a was isolated by distillation as a colourless liquid, b.p. 52–55 °C/0.5 mbar; yield 1.8 g (67%). The isotopic purity of 2a was >98% (D_5 94%, D_4 5%, by 70 eV EI mass spectrometry).

1,1-Bis(trideuteromethyl)-2,2,3,3-tetramethylindan (2b)

This isotopomer was prepared in an analogous manner from phenylmagnesium bromide and [D_6]acetone to give 2-phenyl-1,1,1,3,3,3-hexadeuteropropan-2-ol (63%). Deuterium chloride (generated from dry NaCl and concentrated D_2SO_4) was used to produce the corresponding chloride, 2-chloro-2-phenyl-1,1,1,3,3,3-hexadeuteropropane (80%). From the D_6-labelled chloride (1.55 g, 9.7 mmol), 2,3-dimethylbutene (1.8 g, 21 mmol) and 0.2 cm³ of titanium tetrachloride, 2b was obtained in 70% yield after distillation. No significant loss of label was observed (70 eV EI mass spectrometry).

2,2-Bis(trideuteromethyl)-1,1,3,3-tetramethylindan (2c) and 2-(trideuteromethyl)-1,1,2,3,3-pentamethyl-indan (2d)

These were prepared according to the procedure given for 2 from indan-1,3-diones 1c and 1d. The isotopic purities were >99% (70 eV EI mass spectrometry).

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