Intramolecular Isomerization Reactions of the Molecular Ions of 2-Benzylindanes. The Effect of Substituents on the Rate of Hydrogen Transfer

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The electron impact mass spectra of 1-phenylalkanes and related compounds are normally dominated by two competitive reaction pathways: (i) formally simple cleavage of the C^{α}—C^{β} bond to give $C_7H_7^+$ type ions, and (ii) additional transfer of a hydrogen from the aliphatic chain to give $C_7H_8^{+\cdot}$ type ions.[1] In recent years it has been shown that both reactions are preceded by an intramolecular hydrogen exchange involving mainly H atoms from the γ position of the chain and those from the ortho positions of the aromatic ring.[2–6]

Amongst the examples investigated until now, 1,3-diphenylpropane **1** seems to represent the best molecular system for elucidating the mechanistic details of hydrogen exchange since the energy requirement for dissociation of the C^{γ}—H^{γ} bond is extraordinarily low.[3,4] As a consequence, H^{γ} migration is almost thermoneutral[3] yielding a central intermediate $\mathbf{Z}_{(1)}^{+\cdot}$ (Scheme 1) with a σ– (or Wheland) complex structure. $\mathbf{Z}_{(1)}^{+\cdot}$ can react in three ways, (i) re-formation of the original structure $\mathbf{1}^{+\cdot}$, leading to a partial H^{γ}/H^{ortho} exchange, (ii) cleavage of the C^{α}—C^{β} bond yielding $C_7H_8^{+\cdot}$ daughter ions, and (iii) further isomerization by proton transfer from the σ-complex part of $\mathbf{Z}_{(1)}^{+\cdot}$ to one of the ortho′ positions, yielding $\mathbf{2}^{+\cdot}$ as a second tautomer of $\mathbf{1}^{+\cdot}$. As *both* isomerizations $\mathbf{1}^{+\cdot} \rightleftharpoons \mathbf{Z}_{(1)}^{+\cdot}$ and $\mathbf{Z}_{(1)}^{+\cdot} \rightleftharpoons \mathbf{2}^{+\cdot}$ are nearly thermoneutral, the $H^{ortho}/H^{ortho'}$ exchange is as important as the H^{γ}/H^{ortho} exchange.[4]

To exclude $H^{ortho}/H^{ortho'}$ exchange, which combines the H^{γ}/H^{ortho} and $H^{\alpha}/H^{ortho'}$ exchange sets in $\mathbf{1}^{+\cdot}$, and to simplify analysis of the isomerization, studies have been extended to 2-benzylindane (**3**).[7] As compared with $\mathbf{1}^{+\cdot}$, the benzo nucleus in $\mathbf{3}^{+\cdot}$ should not be able to act as an acceptor for the H^{α} atoms (and for a proton from the intermediate $\mathbf{Z}_{(3)}^{+\cdot}$, cf. Scheme 2) but maintains its strongly activating effect on the C^{γ}—H^{γ} bonds of the five-membered ring. Thus, the isomerization of $\mathbf{3}^{+\cdot}$ is expected to be described simply in terms of *one* H^{γ}/H^{ortho} exchange set.

It has been shown, by introducing methoxy substituents into the aromatic

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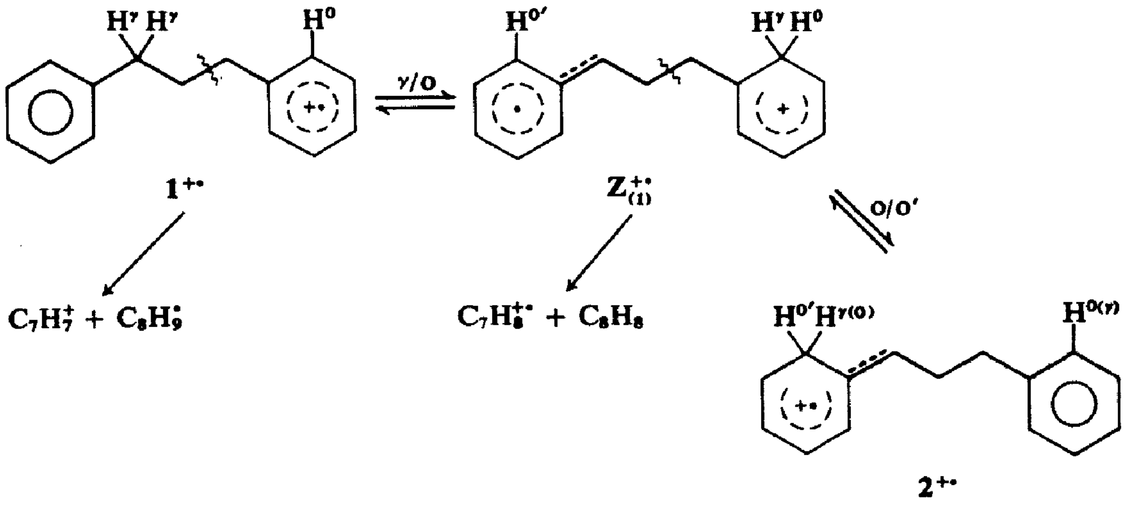
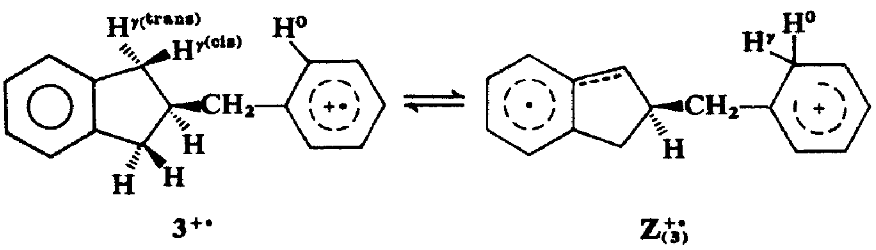


Scheme 1



Scheme 2

nuclei of **1**, that the relative abundances of $C_7H_7^+$ ($C_7H_6OCH_3^+$) and $C_7H_8^{+\bullet}$ ($C_7H_7OCH_3^{+\bullet}$) ions depend sensitively on the heat of isomerization, ΔH_r ($\mathbf{1}^{+\bullet} \rightleftharpoons Z_{(1)}^{+\bullet}$), suggesting the existence of an isomerization equilibrium between $\mathbf{1}^{+\bullet}$ and $Z_{(1)}^{+\bullet}$.[3] Hence, in the present work, the effect of OCH_3 substituents on the relative abundances of $C_7H_6X^+$ and $C_7H_7X^{+\bullet}$ ions and on the rate of H^{γ}/H^{ortho} exchange has been investigated for the simpler 2-benzylindane system.

EXPERIMENTAL

Synthesis of the various 2-benzylindanes was carried out by condensing the appropriate benzaldehyde with 1-indanone to give the corresponding chalcone derivatives which were hydrogenated stepwise to the corresponding 2-benzylindan-1-ones and 2-benzylindan-1-ols. The latter were dehydrated with aqueous formic acid or dimethylsulfoxide to give the corresponding 2-benzylindenes which were hydrogenated or deuterated with $RhCl[P(C_6H_5)_3]_3/C_6H_6$ to give the corresponding 2-benzylindanes. The indanyl-d_5 analogues **3b**, **4b**, and **5b** were obtained by repeated basic H/D exchange of the 2-benzylindenes, which afforded the corresponding 2-benzyl-[1,1,3-D_3]indenes, and further deuteration by homogeneous catalysis. The ring-labelled analogues **4a** and **5a** were obtained by cleavage of the unlabelled precursors to the corresponding phenols which were subjected to repeated basic H/D exchange. The resulting deuterated phenols were re-methylated with diazomethane. The compounds were purifed by recrystallization or distillation and were characterized by mass, ^{1}H-NMR and IR spectrometry. Full details of the synthetic work will be described elsewhere.

The deuterium content of the labelled compounds was: (**3a**) 95.9% d_5, 4.1% d_4; (**3b**) 87.1% d_5, 1.2% d_6, 11.1% d_4, 0.6% d_3; (**3c**) 96.9% d_2, 2.2% d_1, 0.9% d_0; (**4a**) 96.3% d_2, 1.4% d_3, 1.9% d_1, 0.4% d_0; (**4b**) 88.8% d_5, 10.7% d_4; 0.5% d_3; (**5a**) 95.3% d_3, 4.0% d_2; 0.7% d_1; (**5b**) 84.4% d_5, 14.3% d_4, 1.0% d_3, 0.3% d_2; (**5c**) 88.8% d_3, 9.0% d_2, 1.9% d_1, 0.3% d_0.

The 70 eV mass spectra (Fig. 1) were measured with a Varian MAT 311A instrument with usual conditions.[3,4] The MIKE spectra (Fig. 2), as well as the partial 70 eV, 11(12) eV and MIKE (70 eV) spectra, were measured with a Vacuum Generators ZAB-2F instrument (septum inlet 220–240°C, ion source

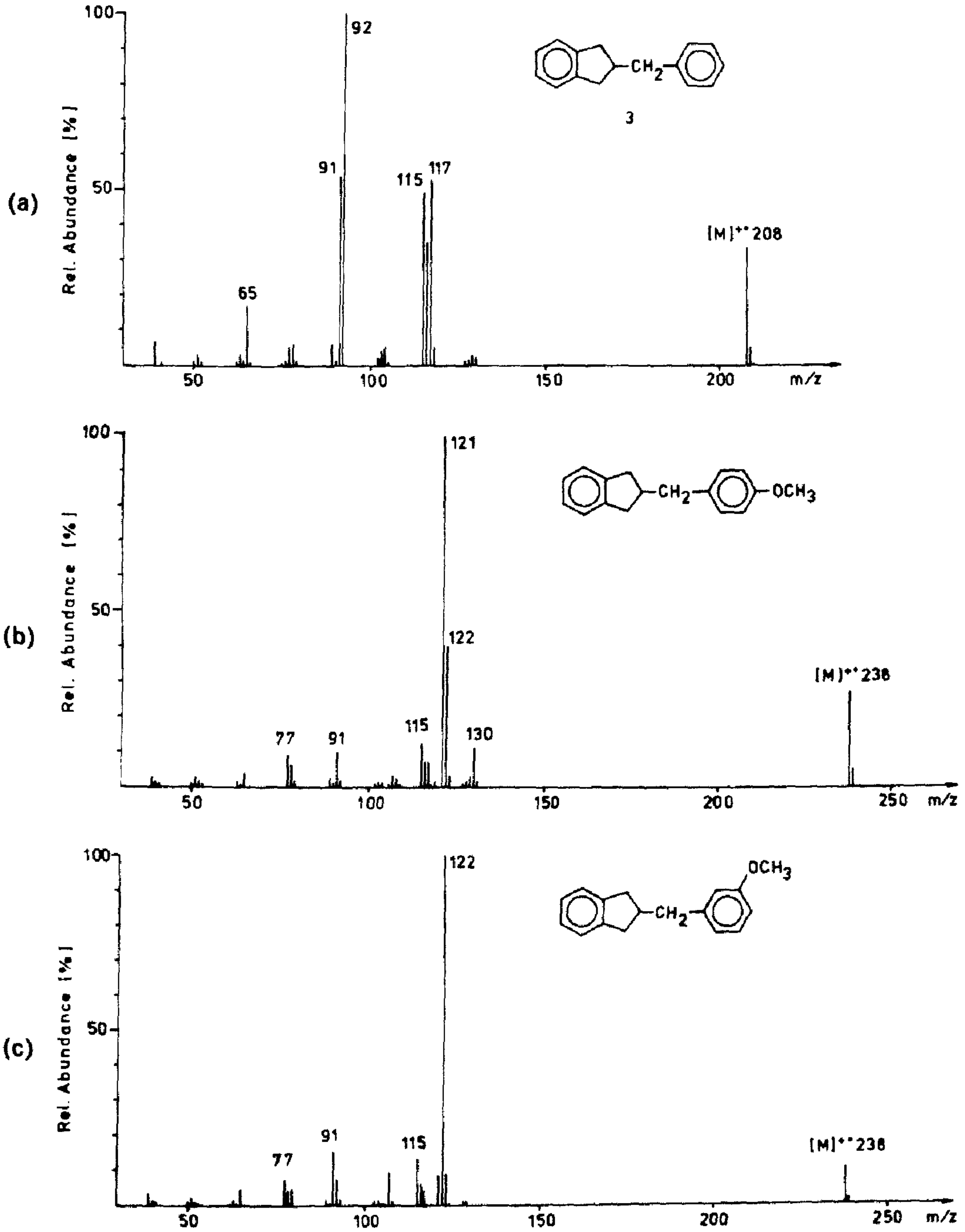
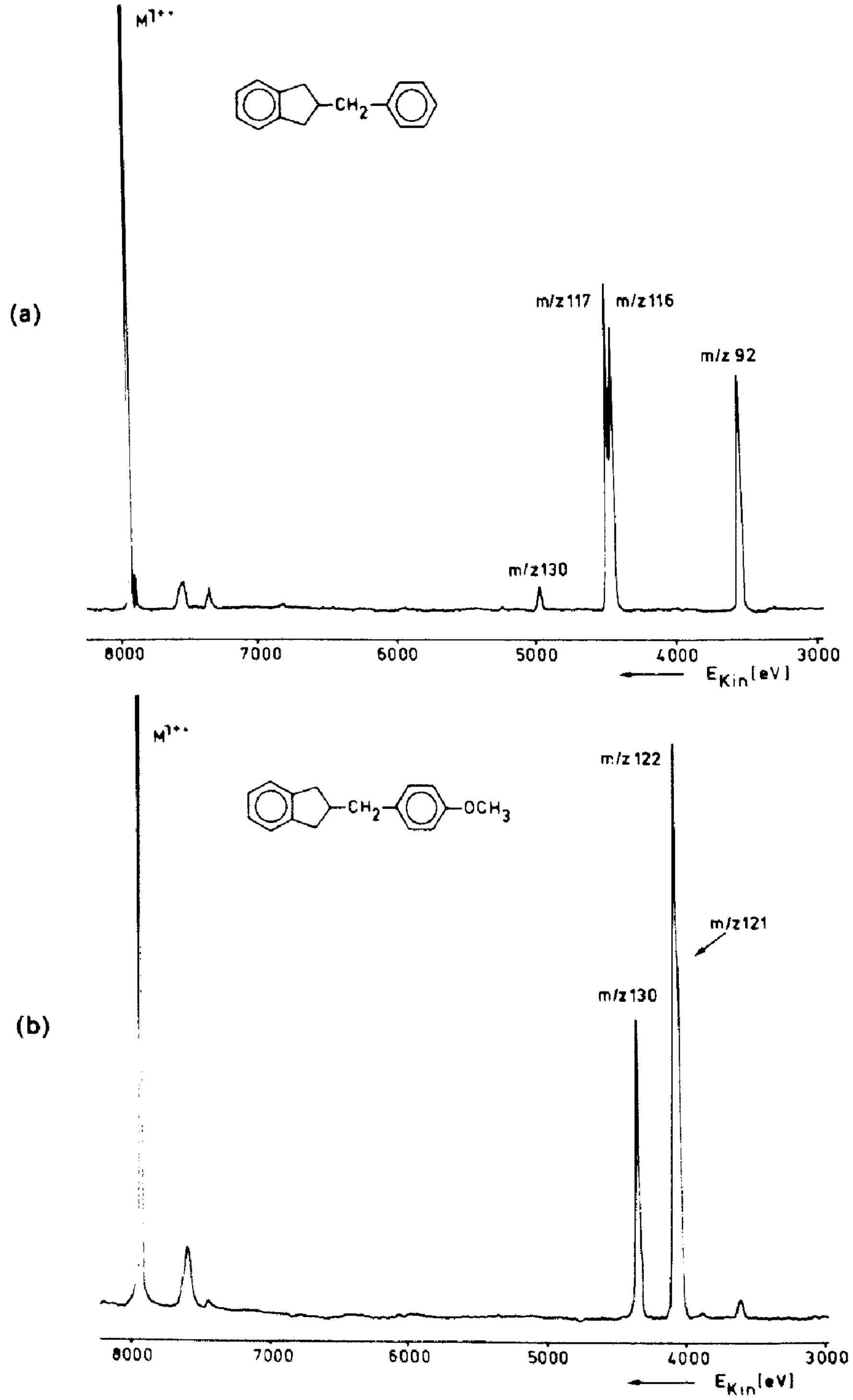


Fig. 1. 70 eV mass spectra of 2-benzylindanes (a) **3**, (b) **4** and (c) **5**.

temperature 140°C, trap current 200 μA, nominal ion source pressure 2–5 × 10^{-7} torr). The low eV measurements were carried out at zero repeller potential, the eV scale being adjusted to I(benzene) ≡ 9.5 eV.

70 eV and Metastable Spectra of 2-Benzylindanes

The 70 eV mass spectra of 2-benzylindane (**3**), 2-(*para*-methoxybenzyl)-indane (**4**), and 2-(*meta*-methoxybenzyl)-indane (**5**) are given in Fig. 1. The abundance ratio [$C_7H_7^+$]/[$C_7H_8^{+\cdot}$] for **3** (Fig. 1(a)) is very similar to that observed for **1**.[3,4] Moreover, as found for the 1,3-diphenylpropane system,[3] a



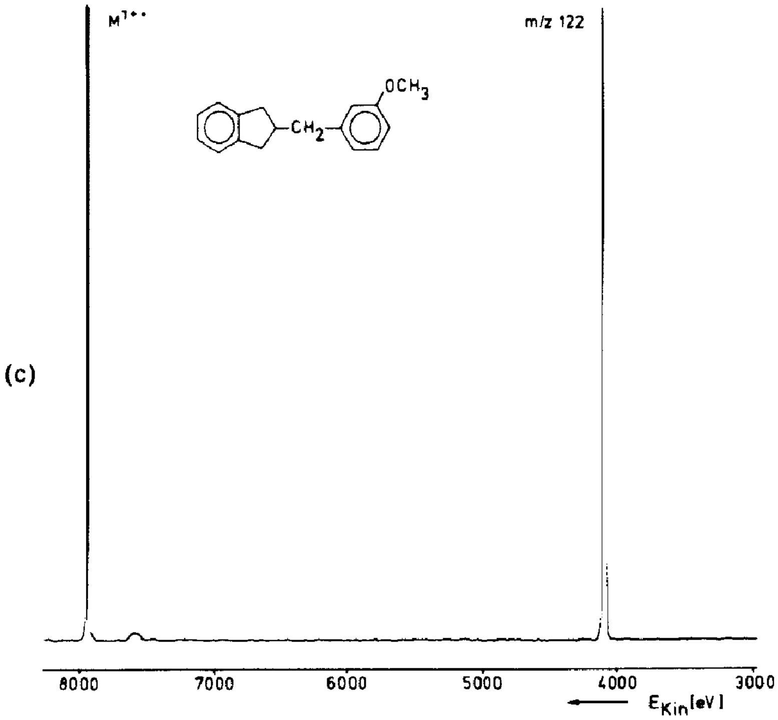


Fig. 2. MIKE spectra of 2-benzylindanes (a) **3**, (b) **4** and (c) **5**.

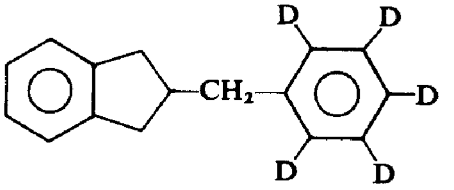
meta-OCH_3 group (Fig. 1(c)) strongly favours the formation of the rearrangement ion $C_7H_7OCH_3^{+\bullet}$ (*m/z* 122), suppressing the 'simple cleavage' to $C_7H_6OCH_3^+$ ions (*m/z* 121). As expected, the *para*-OCH_3 substituent leads to $C_7H_6OCH_3^+$ as the base peak. However, contrary to that found with **1**, rearrangement fragments are still formed to a considerable degree. This difference between the fragmentation behaviour of *para* OCH_3-substituted $\mathbf{1}^{+\bullet}$ and $\mathbf{3}^{+\bullet}$ molecular ions is discussed later.

Besides $C_7H_6X^+$ and $C_7H_7X^{+\bullet}$ ions, $\mathbf{3}^{+\bullet}$, $\mathbf{4}^{+\bullet}$ and $\mathbf{5}^{+\bullet}$ form abundant $C_9H_7^+$, $C_9H_8^{+\bullet}$ and $C_9H_9^+$ ions (*m/z* 115–117), originating from the indanyl moieties, the last two being due to primary fragmentation processes in competition with formation of $C_7H_6X^+$ and $C_7H_7X^{+\bullet}$. A further characteristic elimination reaction of the *para*-isomer $\mathbf{4}^{+\bullet}$ is loss of anisole yielding *m/z* 130 (Fig. 1(b)).

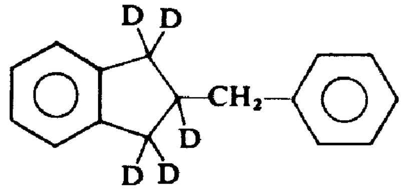
The fragmentation of the metastable molecular ions of **3**, **4** and **5** is illustrated by their MIKE spectra in Fig. 2. From $\mathbf{3}^{+\bullet}$ (Fig. 2(a)), $C_7H_8^{+\bullet}$, $C_8H_8^+$ and $C_8H_9^+$ ions (*m/z* 92, 116 and 117, respectively) are formed with similar abundances, $C_7H_7^+$ and $C_9H_7^+$ being suppressed for energetic reasons. In the MIKE spectra of $\mathbf{4}^{+\bullet}$ and $\mathbf{5}^{+\bullet}$, the main fragment ions originate from the methoxybenzyl part (Fig. 2(b) and 2(c)). It is interesting to note that the $C_7H_7OCH_3^{+\bullet}$ rearrangement ions (*m/z* 122) give the base peak in the MIKE spectrum of $\mathbf{4}^{+\bullet}$ in spite of the unfavourable position of the OCH_3 substituent. Finally, metastable $\mathbf{5}^{+\bullet}$ ions yield the rearrangement ions $C_7H_7OCH_3^{+\bullet}$ as the single product (Fig. 2(c)), as expected from the 70 eV spectrum.

H^{γ}/H^{ortho} Exchange in $\mathbf{3}^{+\bullet}$, $\mathbf{4}^{+\bullet}$ and $\mathbf{5}^{+\bullet}$

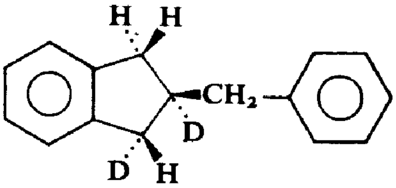
The 70 eV and 11 eV partial[8] mass spectra of **3** and its pentadeuterated analogues **3a** and **3b** as well as of the stereospecifically deuterated analogue **3c**



3a



3b



3c

TABLE 1
Partial 70 eV, 11 eV and MIKE spectra of 2-benzylindanes **3–3c**[a]

m/z		89	90	91	92	93	94	95	96	97
(**3**)	70 eV	3.3	0.4	28.2	68.2	—	—	—	—	—
	11.0 eV	—	—	1.2	98.9	—	—	—	—	—
	2nd ffR	—	—	(<0.3)	100.0	—	—	—	—	—
(**3a**)	70 eV	2.7	0.4	9.3	1.7	0.6	0.7	4.2	22.8	57.7
	11.0 eV	—	—	—	—	—	—	0.7	23.4	75.9
	2nd ffR	—	—	—	—	—	—	3.6	50.5	45.9
(**3b**)	70 eV	0.4	0.6	8.7	11.3	63.1	10.5	4.4	1.0	—
	11.0 eV	—	—	0.7	2.3	72.0	24.3	0.7	—	—
	2nd ffR	—	—	—	(<0.5)	45.0	50.1	4.9	—	—
(**3c**)	70 eV	1.3	1.3	16.8	75.0	5.4	0.2	—	—	—
	11.0 eV	—	—	2.3	94.8	2.9	—	—	—	—
	2nd ffR	—	—	—	87.5	12.5	—	—	—	—

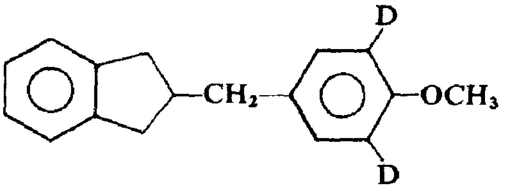
[a] In $\%\Sigma[F]^+$, corrected for natural content of $^{13}C_2$, and, approximately, for incomplete D labelling.

are given in Table 1, together with data for the corresponding longer-lived metastable molecular ions.

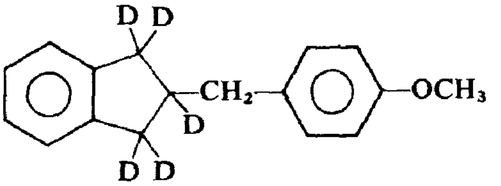
It is important to note that at 70 eV about 33% of $C_7H_7^+$ ions originate from the indanyl group of the molecular ions (cf. *m/z* 91 from **3a**). Hence, the interpretation of the 70 eV spectra of **3b** is complicated by the contribution of $C_7(H,D)_7^+$ at *m/z* 96, 95 and 94.[9] Assuming stereospecific transfer of the H^{cis} and D^{cis} atoms in $\mathbf{3a}^{+\cdot}$ and $\mathbf{3b}^{+\cdot}$ respectively, and neglecting isotope effects, $C_7H_8^{+\cdot}$ ions from **3** are split into about 85% $C_7H_3D_5^{+\cdot}$ (*m/z* 97) and 15% $C_7H_4D_4^{+\cdot}$ (*m/z* 96) from **3a** and, correspondingly, approximately 85% $C_7H_7D^{+\cdot}$ (*m/z* 93) and 15% $C_7H_6D_2^{+\cdot}$ (*m/z* 94) from **3b**.[9] Thus, a considerable proportion of $\mathbf{3}^{+\cdot}$ molecular ions undergo H^{γ}/H^{ortho} exchange within a lifetime of $\ll 10^{-6}$ s.

By using 11 eV electrons and sampling the fragment ions formed in the ion source, the extent of H^{γ}/H^{ortho} exchange can be studied for longer-lived molecular ions (lifetime $\lesssim 10^{-6}$ s). The results (Table 1) reveal that the abundance ratios $[C_7H_4D_4^{+\cdot}]/[C_7H_3D_5^{+\cdot}]$ from **3a** and $[C_7H_6D_2^{+\cdot}]/[C_7H_7D^{+\cdot}]$ from **3b** have increased to about 25:75. In the corresponding metastable molecular ions (formed by 70 eV ionization), H^{γ}/H^{ortho} exchange increases much more due to their lifetimes of around 10^{-5} s. The values found are near unity, being the ratio for complete randomization of the four H(D) atoms at the γ(cis) and the ortho positions.

The 11 eV data for compound **3c** bearing a D atom *trans* to the benzyl group clearly show that H^{γ} transfer occurs from the *cis* positions of the indanyl ring with a high degree of stereospecificity. This holds at least for the molecular ions formed with 11 eV electrons but it seems to be valid also for the unstable ions formed at 70 eV and even for the metastable molecular ions. For the latter, the situation seems more complex due to a stereochemically non-specific contribution which could be assigned to opening reactions of the indanyl ring occurring in highly excited molecular ions of the *unsubstituted* 2-benzylindanes (cf. compound **5c**).

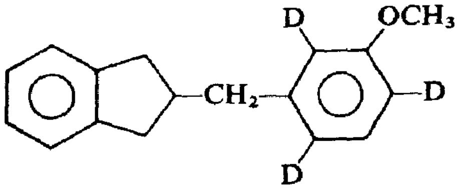


4a

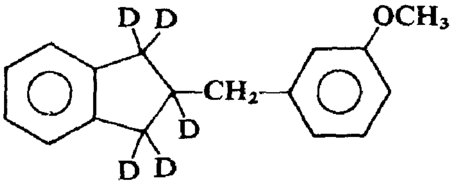


4b

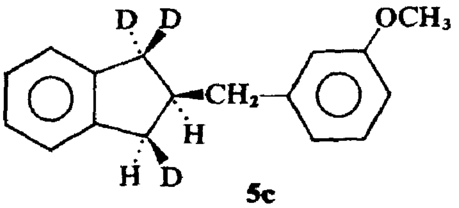
A similar, time-dependent H^{γ}/H^{ortho} exchange is found to occur in *para*-substituted molecular ions $\mathbf{4}^{+\cdot}$ (Table 2). Assuming stereospecific D^{cis} transfer, the ratios of abundances at *m/z* 123 and *m/z* 124 in the partial spectra of **4b** reflect a considerably decreased rate of H^{γ}/H^{ortho} exchange prior to formation of $C_7(H,D)_7OCH_3^{+\cdot}$ ions.[10] For molecular ion lifetimes $\ll 10^{-6}$ s, the ratio [124]/[123] is only 5:95, increasing slightly to 13:87 for lifetimes $\lesssim 10^{-6}$ s (12 eV) and 27:73 for metastable molecular ions. The data for **4a** labelled in positions *meta* to the CH_2 group exclude convincingly any skeletal (ring expansion) isomerization in the ionized para-methoxybenzyl group.[11] Moreover, proton shifts ('ring walks') at the level of the corresponding σ-complex intermediate (cf. $\mathbf{Z}_{(3)}^{+\cdot}$, Scheme 2) are clearly ruled out for all ranges of internal energies, in accordance with earlier results[3] for $\mathbf{Z}_{(1)}^{+\cdot}$ (Scheme 1).



5a



5b



5c

Contrary results found for $\mathbf{4}^{+\cdot}$, an increased rate of H^{γ}/H^{ortho} exchange is found for the *meta* isomer $\mathbf{5}^{+\cdot}$ (Table 3). For 70 eV unstable molecular ions the abundance ratio [124]/[123] is 20:80 for $\mathbf{5b}^{+\cdot}$ and $\mathbf{5c}^{+\cdot}$, for example, increasing to 40:60 at 11 eV and 50:50 for the metastable ions. The latter ratio is in exact agreement with the ratio expected for complete randomization of the four H atoms at the *ortho* and *cis* positions of $\mathbf{5}^{+\cdot}$.

The very close concordance of the data for **5b** and the stereospecifically labelled analogue **5c** provides compelling evidence for a stereospecific H^{cis}/H^{ortho} exchange. Contrary to the case of $\mathbf{3}^{+\bullet}$, cleavage of the indanyl ring of $\mathbf{5}^{+\bullet}$ can be excluded, probably due to localization of charge in the anisyl moiety. Finally, it should be noted that no isotope effect is observed for metastable $\mathbf{5}^{+\bullet}$ ions, suggesting that H^{γ}/H^{ortho} transfer is *not* a rate-determining isomerization process.

TABLE 2
Partial 70 eV, 12 eV and MIKE spectra of 2-(*para*-methoxybenzyl)-indanes **4–4b**[a]

m/z		121	122	123	124
(4)	70 eV	80.7	19.3	—	—
	12.0 eV	51.1	48.9	—	—
	2nd ffR	33.9	66.1	—	—
(4a)	70 eV	—	(<0.3)	79.1	20.9
	12.0 eV	—	(<0.5)	53.8	46.2
	2nd ffR	—	(<0.5)	34.9	65.1
(4b)	70 eV	71.2[b]	10.2[b]	17.7	0.9
	12.0 eV	32.9	20.6	40.7	5.9
	2nd ffR	25.1	9.6	53.8	11.6

[a] See footnote to Table 1.
[b] See Ref. 10.

TABLE 3
Partial 70 eV, 11 eV and MIKE spectra of 2-(*meta*-methoxybenzyl)-indanes **5–5c**[a]

m/z		121	122	123	124	125
(5)	70 eV	7.9	92.1	—	—	—
	11.0 eV	0.3	99.7	—	—	—
	2nd ffR	—	100.0	—	—	—
(5a)	70 eV	—	—	<1.5	23.1	75.4
	11.0 eV	—	—	(<0.1)	39.4	60.6
	2nd ffR	—	—	(<0.4)	50.1	49.9
(5b)	70 eV	2.5[b]	7.2[b]	70.3	20.1	—
	11.0 eV	—	2.8	58.1	38.1	—
	2nd ffR	—	—	49.9	50.1	(<0.4)
(5c)	70 eV	9.7[b]	0.4	71.3	18.6	—
	11.0 eV	—	(<0.2)	58.0	42.0	—
	2nd ffR	—	—	50.2	49.8	(<0.4)

[a] See footnote to Table 1.
[b] See Ref. 10.

CONCLUSIONS

Effect of Ion Lifetime on the Rate of H^{γ}/H^{ortho} Exchange

Comparison of experimental abundance ratios with those calculated for simple four-hydrogen exchange in $\mathbf{3}^{+\bullet}$, $\mathbf{4}^{+\bullet}$ and $\mathbf{5}^{+\bullet}$ (Fig. 3) yields a mean number

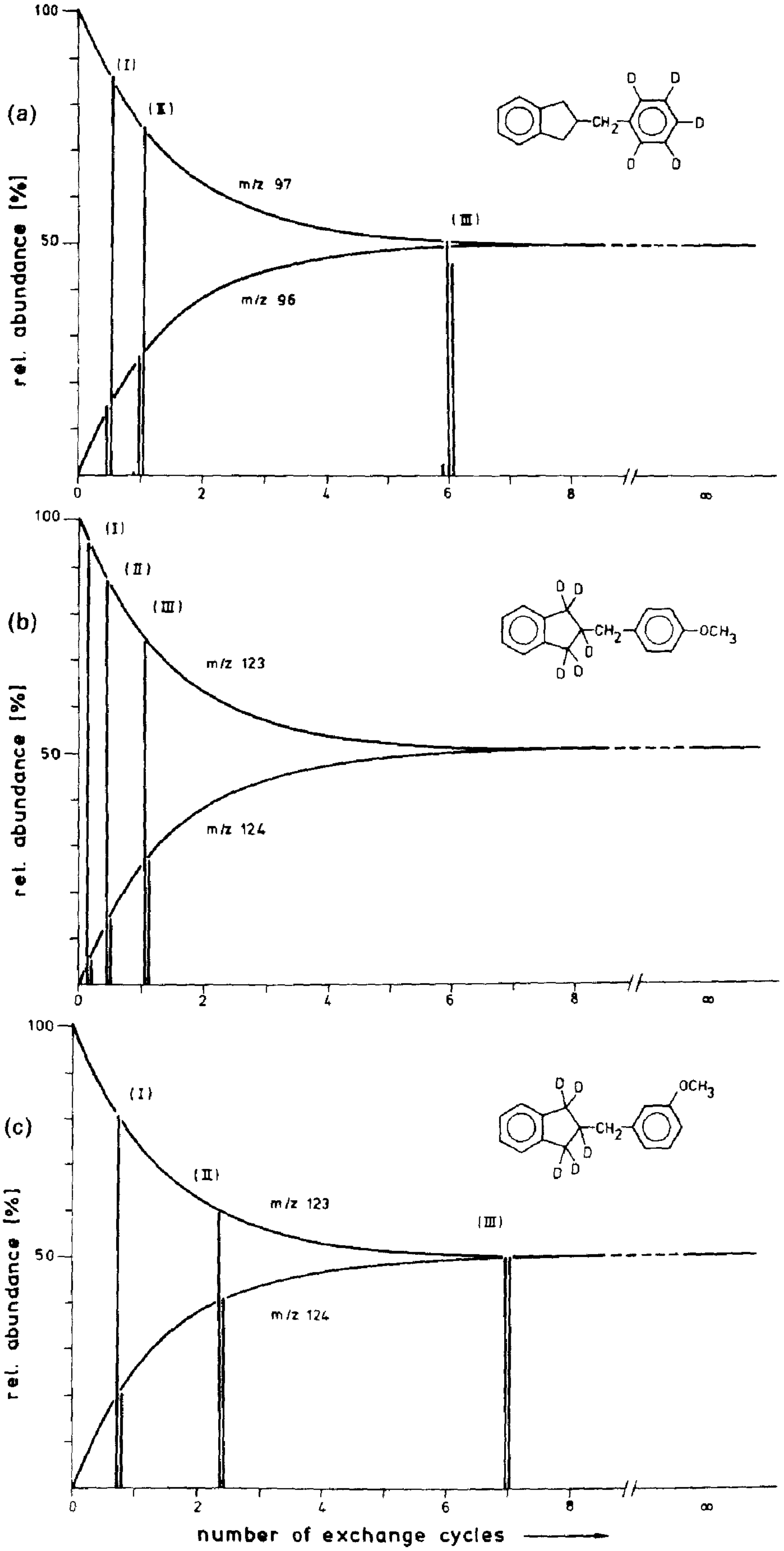


Fig. 3. Abundance ratios calculated as a function of the number of exchange cycles in (a) **3a**$^{+\cdot}$, (b) **4b**$^{+\cdot}$ and (c) **5b**$^{+\cdot}$, and corresponding $C_7(H,D)_7X^{+\cdot}$ abundance distributions observed for molecular ion lifetimes of (I) $\ll 10^{-6}$ s, (II) $\lesssim 10^{-6}$ s and (III) $\sim 10^{-5}$ s.

(n) of exchanges (e.g. the two steps $\mathbf{3}^{+\cdot} \rightarrow \mathbf{Z}_{(3)}^{+\cdot} \rightarrow \mathbf{3}^{+\cdot}$) as a quantitative measure for the degree of H^{γ}/H^{ortho} exchange. The data are collected in Table 4 and contrasted to the results of field ionization measurements[12] and earlier data on $\mathbf{3}^{+\cdot}$[7] and $\mathbf{1}^{+\cdot}$.[4]

It is evident that H^{γ}/H^{ortho} exchange is much slower than simple H^{γ} transfer. The minimum lifetime necessary to achieve an H^{γ}/H^{ortho} exchange can be estimated from Table 4 to be $\geq 10^{-8}$ s in accordance with FIK results on simple 1-phenylalkanes.[13] As compared with $\mathbf{1}^{+\cdot}$,[4] H^{γ}/H^{ortho} exchange in $\mathbf{3}^{+\cdot}$ seems to be slightly faster (70 eV and metastable region). This may result from (i) the fact that only four H atoms are involved instead of the eight in $\mathbf{1}^{+\cdot}$ and (ii) a lower activation entropy (higher frequency factor) for H transfer in $\mathbf{3}^{+\cdot}$ as compared with $\mathbf{1}^{+\cdot}$. The latter argument is supported by FIK measurements[12] revealing that, at very short lifetimes, $C_7H_8^{+\cdot}$ is formed in much higher relative yields from $\mathbf{3}^{+\cdot}$ than from $\mathbf{1}^{+\cdot}$. Similarly, the enhanced relative abundance of $C_7H_7OCH_3^{+\cdot}$ from **4** (Fig. 1(b)), as compared with that found for 1-(*para*-methoxybenzyl)-3-phenylpropane[3] may be due to entropic reasons.

TABLE 4
Number of exchange cycles in the molecular ions of 2-benzylindanes **3–5** and of 1.3-diphenyl-propane **1** as function of ion lifetime $\bar{\tau}$

	ZAB-2F			MAT 311A	
$\bar{\tau}$ [s]	$\mathbf{3}^{+\cdot}$	$\mathbf{4}^{+\cdot}$	$\mathbf{5}^{+\cdot}$	$\mathbf{3}^{+\cdot}$	$\mathbf{1}^{+\cdot}$
$\leq 10^{-9}$ (FIK)	—	—	—	0	0
$\ll 10^{-6}$ (70 eV ion source)	0.5	0.2	0.8	0.8	$\sim$0.6
$\lesssim 10^{-6}$ (11 or 12 eV ion source)	1.0	0.5	2.5	1.3	$\sim$3
$\sim 10^{-5}$ 2nd ffR	$\geq$6	1.1	$\geq$7	$\geq$7	$\sim$6

Effect of Substituents on the Rate of H^{γ}/H^{ortho} Exchange

The substituent effect of the OCH_3 group on the rate of H^{γ}/H^{ortho} exchange in $\mathbf{3}^{+\cdot}$ can be attributed to its specific influence on the isomerization equilibrium between $\mathbf{3}^{+\cdot}$ and $\mathbf{Z}_{(3)}^{+\cdot}$ (Fig. 4).[3] Stabilization of the former by OCH_3 does not depend significantly on the site of substitution. The σ-complex intermediate is strongly stabilized only by a *meta* OCH_3 group being *para* or *ortho* to the protonated CH group of the ring. Since a *para* OCH_3 group does stabilize $\mathbf{3}^{+\cdot}$ but not $\mathbf{Z}^{+\cdot}$ isomerization $\mathbf{4}^{+\cdot} \leftrightarrows \mathbf{Z}_{(4)}^{+\cdot}$ becomes highly endothermic whereas $\mathbf{5}^{+\cdot} \rightleftarrows \mathbf{Z}_{(5)}^{+\cdot}$ remains thermoneutral or becomes slightly exothermic ($\Delta H_f[\mathbf{Z}_{(4)}^{+\cdot}] - \Delta H_f[\mathbf{Z}_{(5)}^{+\cdot}] \approx 20$ kcal mole^{-1}).[14,3]

From this it follows that *metastable* $\mathbf{3}^{+\cdot}$ and $\mathbf{5}^{+\cdot}$ ions must be able to pass across the isomerization barrier several times thereby equilibrating their H^{cis} and H^{ortho} atoms prior to fragmentation via $\mathbf{Z}_{(3)}^{+\cdot}$ and $\mathbf{Z}_{(5)}^{+\cdot}$, respectively. Shorter-lived $\mathbf{3}^{+\cdot}$ and $\mathbf{5}^{+\cdot}$ ions do not reach statistical randomization within their lifetimes, more or less of them 'flying' over the $\mathbf{Z}^{+\cdot}$ minima towards fragmentation without entering the $\mathbf{Z}^{+\cdot}$ energy valley. In the case of $\mathbf{5}^{+\cdot}$, the $\mathbf{Z}_{(5)}^{+\cdot}$ minimum is

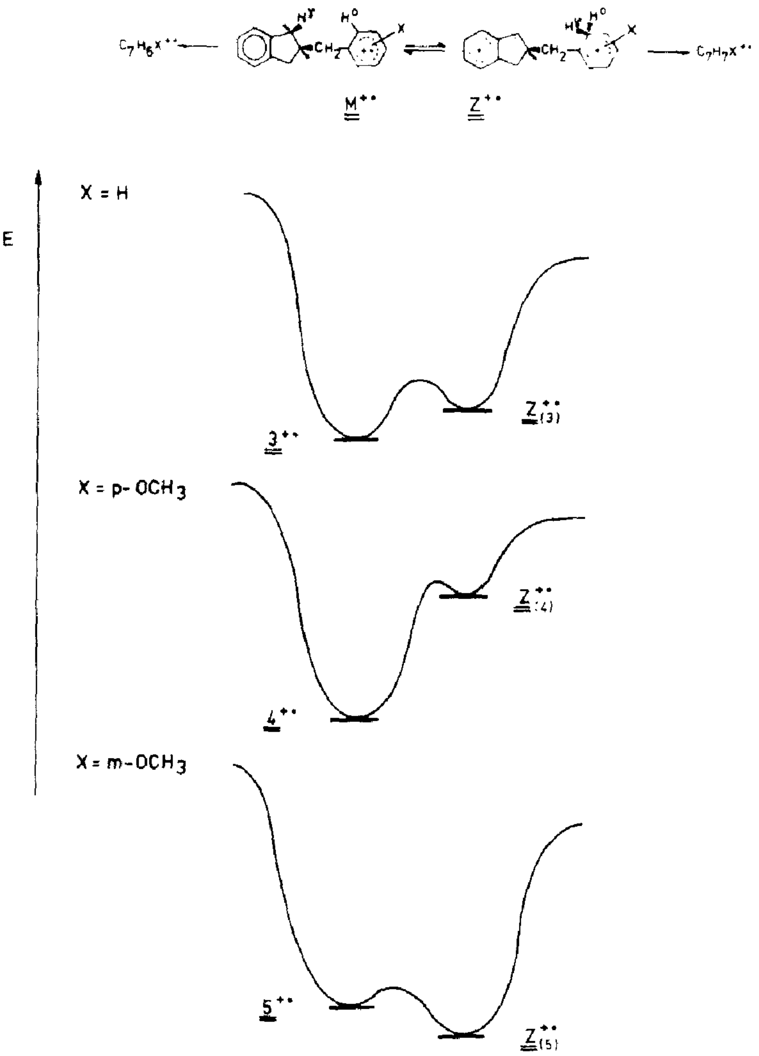


Fig. 4. Effect of *para* and *meta* OCH_3 substituents on the isomerization equilibrium of $\mathbf{3}^{+\cdot}$, $\mathbf{4}^{+\cdot}$ and $\mathbf{5}^{+\cdot}$ (qual.).

more 'attractive' even for higher excited ions than is the corresponding $\mathbf{Z}_{(3)}^{+\cdot}$ minimum starting from $\mathbf{3}^{+\cdot}$. On the other hand, since the $\mathbf{Z}_{(4)}^{+\cdot}$ minimum is much less pronounced and not far from threshold of fragmentation even *metastable* $\mathbf{4}^{+\cdot}$ ions, on average, 'return' only *once* from above $\mathbf{Z}_{(4)}^{+\cdot}$ energy valley ($n = 1$, Table 4) prior to fragmentation.

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8. Analysis of the *m/z* 115–117 range is complicated due to non separable isotopomer clusters but is in qualitative agreement with the following results.
9. Assuming complete randomization of H and D atoms during the secondary fragmentation $C_9H_4D_5^+ \rightarrow C_7H_{2+x}D_{5-x}^+ + C_2H_{2-x}D_x$ $(0 \leq x \leq 2)$.[7]
10. For **4b** as well as for **5b** and **5c** $C_9(H,D)_9^+$ and $C_9(H,D)_8^{+\bullet}$ ions may interfere partially at *m/z* 121 and *m/z* 122.
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