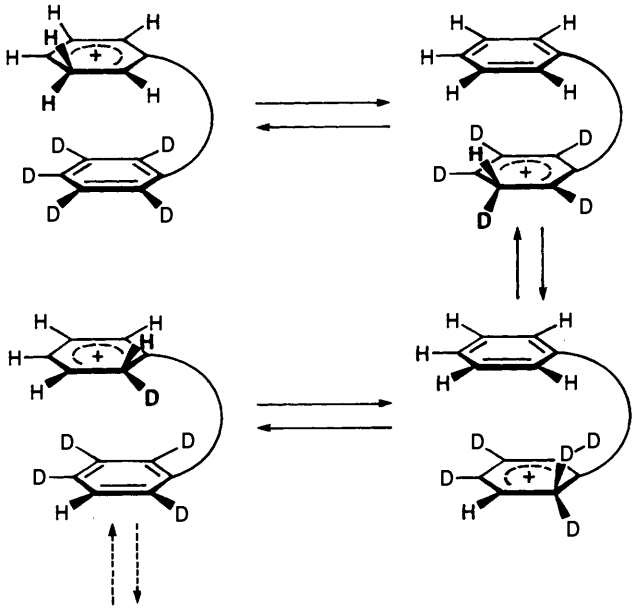
Fast Interannular Proton Transfer in Gaseous Protonated α,ω-Diphenylalkanes: Stereocontrol by the Cyclohexane-1,4-diyl Unit†

Dietmar Kuck,* Detlef Thölmann, and Hans-Friedrich Grützmacher
Fakultät für Chemie, Universität Bielefeld, Universitätsstraße 25, D-4800, Bielefeld 1, FRG

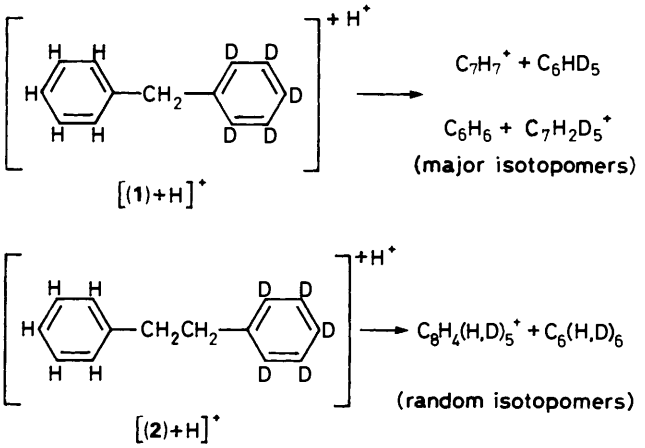
The fast ring-to-ring proton transfer in protonated 1,4-bis(ω-phenylalkyl)cyclohexanes [(**5a**) + H]$^+$, [(**5b**) + H]$^+$, and [(**6**) + H]$^+$ has been studied by chemical ionization mass spectrometry. The cyclohexane-1,4-diyl unit exerts a distinct stereocontrol upon the rate of proton exchange. Complete proton equilibration is found for protonated *cis*-dibenzylcyclohexane [(**5a**) + H]$^+$, whereas in the *trans* isomer [(**5b**) +H]$^+$ the interannular proton transfer is strongly decelerated. The *trans*-bis(β-phenylethyl) homologue [(**6**) + H]$^+$ is found to represent an intermediate case. By comparison with simpler protonated diphenylalkanes the rate of the interannular proton transfer for metastable ions [(**5b**) +H]$^+$ and [(**6**) + H]$^+$ is estimated to lie within the limits 5 × 10^5 and 10^6 s^{-1}.

The interannular proton transfer reactions between two or more benzene rings of gaseous protonated long-chain α,ω-diphenylalkanes[2] and oligophenylalkanes[3] are particularly fast processes, leading to complete equilibration of up to 21 protons within a few microseconds. The overall mechanism of the proton exchange consists of extremely fast *intra*annular hydride shifts within the protonated ring combined with fast consecutive *inter*annular proton transfer steps:



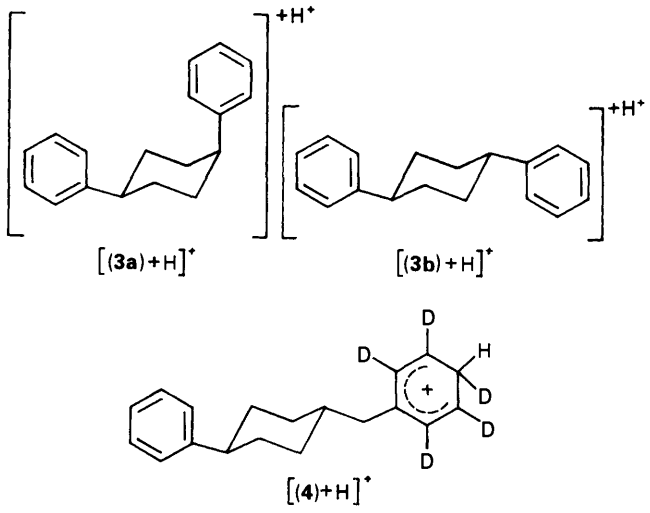
The major fragmentation pathway of protonated α,ω-diphenylalkanes is the loss of C_6H_6, *i.e.*, protonolysis of either of the C^{α}–C^{ipso} or the C^{ω}–$C^{ipso'}$ bond to give a neutral benzene fragment. For metastable [M + H]$^+$ ions, this is the only fragmentation pathway. The elements of the aliphatic link between the rings are completely retained in the ionic fragment [M + H − C_6H_6]$^+$.[2,4,5] In the case of the [ring-$^2H_5$]-labelled analogues, loss of each 50% C_6H_6 and C_6HD_5 would indicate specific protonolysis without interannular proton (and deuteron) transfer. The other extreme, *viz.* fast interannular equilibration of the six H and five D atoms prior to elimination of benzene, is expected to lead to a statistical distribution of $C_6(H,D)_6$ isotopomers, which is characterized by a convex pattern centred around $C_6H_3D_3$ (43.3%) as the major component. Experimentally, the convex pattern and thus the fast interannular H$^+$ and D$^+$ transfer were found for all protonated α,ω-diphenylalkanes.[2,4,5] Similar behaviour was obtained for various protonated oligophenylalkanes.[3]

Only very few examples have been found so far for a *slow* interannular proton transfer. These are restricted to ions in which the mutual orientation of the donor and acceptor benzene rings does not allow (near) linear C···H···C transition state geometries.[4] In these cases, the interannular proton transfer competes with the fragmentation, which is again loss of benzene, giving rise to a *concave* instead of the otherwise convex pattern for the relative abundances of the various $C_6(H,D)_6$ isotopomers lost from the [ring-$^2H_5$]-labelled [M + H]$^+$ ions. C_6H_6 and C_6HD_5 are eliminated predominantly, but significant contributions of other isotopomers are observed. In addition, the primary isotope effect associated with the interannular H$^+$/D$^+$ transfer becomes evident by a discrimination of the loss of the lighter $C_6(H,D)_6$ isotopomers. This has



Scheme 1.

† See ref. 1.



been demonstrated in detail recently for the fragmentation of protonated [*ring*-$^2H_5$]diphenylmethane, [(**1**) + H]$^+$ (Scheme 1).[4] In contrast, the next higher homologue, protonated [*ring*-$^2H_5$]-1,2-diphenylethane, [(**2**) + H]$^+$, exhibits fast equilibration of the ring H and D atoms, obliterating a possible isotope effect on the interannular proton transfer.

In a search for further examples of *slow* interannular proton-transfer processes we introduced the cyclohexane-1,4-diyl group as a stereocontrolling unit in the aliphatic link between the two benzene rings.

Results and Discussion

Protonated *cis*- and *trans*-1,4-diphenylcyclohexane, [(**3a**) + H]$^+$ and [(**3b**) + H]$^+$, were found to be unsuitable for metastable-ion studies.[6] The elimination of benzene from these α-branched (secondary) benzenium ions is much faster than from unbranched ones[7] and occurs almost completely within the ion source. Thus, the relative abundances of metastable [*M* + H]$^+$ ions that reach the field-free regions of the mass spectrometer are very small; their fragmentation is obscured by that of metastable [*M*]$^{+\cdot}$ and [*M* − H]$^+$ ions, which are also generated in the CI plasma.*

These difficulties were overcome in part in the case of the homologous ions [(**4**) + H]$^+$,[2] which were formed by electron impact (EI) induced fragmentation[5] in order to generate initially *benzyl*-protonated tautomers only. Ions [(**4**) + H]$^+$ exhibit an extremely slow H$^+$ and D$^+$ transfer to the phenyl group without significant exchange but with a marked primary isotope effect.[2,4] Hence, in ions [(**4**) + H]$^+$ both the severe stereocontrol and the ease of protonolysis suppress the interannular proton exchange. Nevertheless, these results suggest that the cyclohexane moiety remains intact during the lifetime of the arenium ions, as is known from many other mass spectrometric fragmentations of stereospecifically substituted cyclohexanes.[8]

In line with these observations, the next higher homologues, *i.e.* ions [(**5a**) + H]$^+$ and [(**5b**) + H]$^+$ as well as ions [(**6**) + H]$^+$, all of them being primary alkylbenzenium ions, were studied successfully (Figure 1).

Throughout this work, arenium ions were generated by chemical ionization (CI)[9] of the neutral hydrocarbons under standard conditions (see the Experimental section). Two scan modes of a double-focussing mass spectrometer (with the magnetic sector preceding the electrostatic one, *i.e.* '*B,E*' configuration) were employed to determine the relative amounts of $C_6(H,D)_6$ isotopomers eliminated from the metastable [*M* + H]$^+$ ions. By selecting the ions of interest at constant magnetic field (*B*) their fragmentation occurring in the field-free region between the magnetic and the electrostatic sector (second FFR) were monitored by scanning the field (*E*) of the latter. The mass-analysed ion kinetic energy spectra (MIKES)[10] obtained in this manner represents all [*M* + H − C_6H_6]$^+$ ions formed in the second FFR and yield information on the proton exchange of particularly long-lived [*M* + H]$^+$ ions (mean lifetime τ = 20–40 μs). Due to single-focussing of the electrostatic sector, MIKE spectrometry generally affords only poor peak resolution with higher precursor-ion masses.

Better resolution is achieved by simultaneous scanning both the *B* and *E* fields at constant *B*/*E* ratios (*B*/*E* linked scan spectra).[10] Under these double-focussing conditions, the fragmentation of the metastable [*M* + H]$^+$ ions that takes place in the field-free region between the ion source and the magnetic sector (first FFR) is monitored. Hence the *B*/*E* linked scan spectra yield information on the proton exchange occurring in the [*M* + H]$^+$ ions of shorter mean lifetimes (τ = 5–10 μs). Therefore, MIKE and *B*/*E* linked scans afford access to different sections of the μs timescale of the ions and, thus, to the extent to which intramolecular isomerization (*e.g.* proton exchange) processes are time dependent.

Again, loss of benzene is the only fragmentation pathway of the metastable ions [(**5a**) + H]$^+$, [(**5b**) + H]$^+$, and [(**6**) + H]$^+$. The MIKE spectra[10] show qualitatively that the interannular proton transfer is fast in the *cis* isomer [(**5a**) + H]$^+$ and rather slow in the *trans* isomer [(**5b**) + H]$^+$. In spite of serious difficulties with overlapping peaks the pattern found for loss of $C_6(H,D)_6$ from ions [(**6**) + H]$^+$ suggests an increase in the proton exchange relative to the lower *trans* homologue [(**5b**) + H]$^+$. The relative abundances of the ions [*M* + H − $C_6(H,D)_6$]$^+$ evaluated from the MIKE spectra had to be corrected for contributions of the corresponding fragment ions of the isobaric metastable precursor ions ($^{13}C_1$)-[*M*]$^{+\cdot}$ and ($^{13}C_2$)-[*M* − H]$^+$; therefore, the uncertainty of these values is high (*ca.* 15–25%), and only the data for ions [(**5b**) + H]$^+$ are given in the Table.

The *B*/*E* linked scan spectra[10] of ions [(**5a**) + H]$^+$, [(**5b**) + H]$^+$, and [(**6**) + H]$^+$ (Figure 1) reflect the stereocontrol effect of the cyclohexane-1,4-diyl unit more clearly. The corrected relative abundances of the fragment ions are collected in the Table. The data are arranged in order of increasing interannular H$^+$/D$^+$ exchange (see, in particular, columns 3 and 8). For comparison, the *B*/*E* linked scan spectra of protonated [$^2H_5$]-labelled diphenylmethane [(**1**) + H]$^+$ and 1,2-diphenylethane [(**2**) + H]$^+$ have been measured and are included in the Table. Whereas in the *cis*-dibenzyl ions [(**5a**) + H]$^+$ the 11 protons and deuterons are fully equilibrated, as in the simpler α,ω-diphenylalkane analogues, they are not in the *trans* isomers [(**5b**) + H]$^+$ and [(**6**) + H]$^+$. The H$^+$/D$^+$ exchange is still relatively fast in the latter, long-chain ion but the rate is markedly reduced for the *trans*-dibenzyl homologue. Both the MIKE and the *B*/*E* linked scan spectra of [(**5b**) + H]$^+$ exhibit a kinetic isotope effect, showing that proton transfer and the elimination of benzene are competing reaction pathways for this ion. This is in qualitative accord with the behaviour of protonated diphenylmethane [(**1**) + H]$^+$ described previously.[4]

The results correspond to the assumption that, according to molecular models, ions [(**5b**) + H]$^+$ have to adopt the energetically less favourable twist or even the boat conformation to achieve a proton transfer between the two rings through a

* For many α,ω-diphenylalkanes the [*M* − H]$^+$ and [*M*]$^{+\cdot}$ ions were found to be considerably more abundant than the corresponding [*M* + H]$^+$ ions. Loss of benzene is the major fragmentation channel of the [*M* − H]$^+$ ions, too.

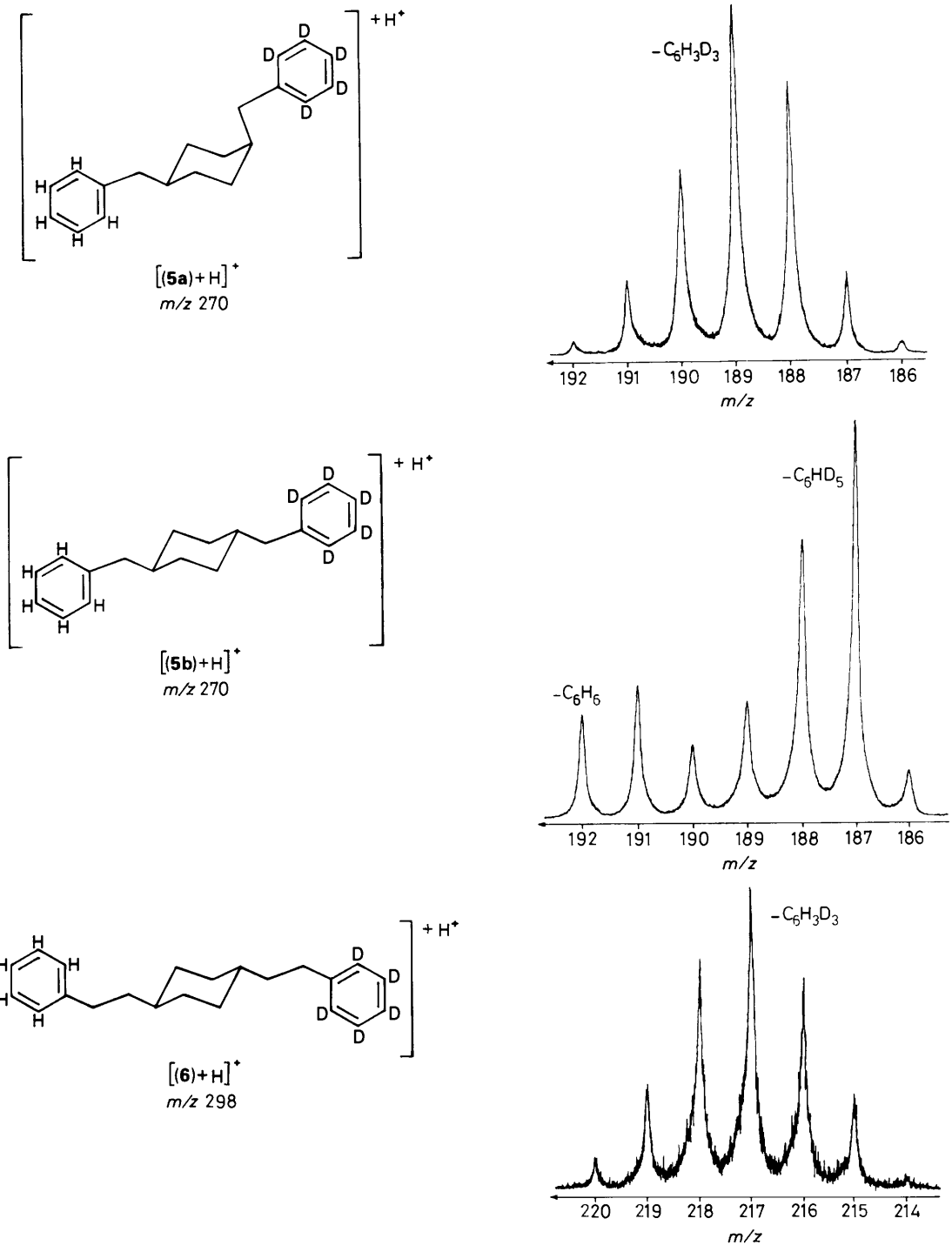


Figure 1. *B*/*E* linked scan mass spectra of protonated 1,4-bis(ω-phenylalkyl)-cyclohexanes (**5a**), (**5b**), and (**6**).

linear or near-linear transition state (Figure 2). In the twist or boat conformations, the benzene rings can find quasi-parallel orientations, similar to protonated 1,ω-diphenylalkanes with $\omega \geq 2$,[2,5] generating several favourable proton donor–acceptor C···H···C arrangements. In contrast with ions [(**5b**) + H]$^+$, both ions [(**5a**) + H]$^+$ and [(**6**) + H]$^+$ can interchange their ring protons in the chair conformation (Figure 2). In the latter case, the limit of the stereocontrol effect of the *trans*-cyclohexane-1,4-diyl unit is reached; higher *trans*-homologues are expected to interchange the eleven ring protons completely prior to fragmentation.

The data in the Table clearly reflect the increasing rate of

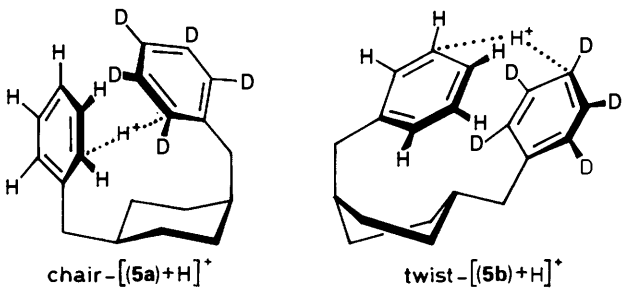


Figure 2.

Table. Benzene isotopomers eliminated from metastable [ring-$^2H_5$] labelled $[M + H]^+$ ions[a].

Ion		C_6H_6	C_6H_5D	$C_6H_4D_2$	$C_6H_3D_3$	$C_6H_2D_4$	C_6HD_5
Calc.	Statistical	0.2	6.5	32.5	43.3	16.2	1.3
[(**2**) + H]$^+$	B/E[b]	0.4	9.2	29.2	39.6	18.8	2.7
[(**5a**) + H]$^+$[c]	B/E	1.2	8.5	30.3	39.1	17.3	3.6
[(**6**) + H]$^+$	B/E	3.5	10.9	24.4	30.9	20.7	9.6
[(**5b**) + H]$^+$	MIKES[d]	6	14	16	18	25	21
[(**5b**) + H]$^+$	B/E	9.9	12.1	6.4	10.3	24.4	36.9
[(**1**) + H]$^+$	B/E	31.2	5.1	0.9	1.2	4.4	57.3
Calc.	Specific	50.0	0.0	0.0	0.0	0.0	50.0

[a] Values given in %Σ; experimental values were corrected for contributions from $^{13}C_2$-$[M - H]^+$ ions. [b] B/E linked scan spectrum, reflecting the fragmentation of the $[M + H]^+$ ions in the first field-free region of the mass spectrometer.[10] [c] Values not corrected for contents of ≤10% of (**5b**) (see the Experimental section). [d] MIKE spectrum, reflecting the fragmentation in the second field-free region of the mass spectrometer.[10] The uncertainty of these values is unusually high (rel. ±15%), see text. For MIKES data of [(**1**) + H]$^+$ and [(**2**) + H]$^+$, see refs. 2 and 4.

the interannular proton transfer, including those of the simple protonated diphenylalkanes [(**2**) + H]$^+$ and [(**1**) + H]$^+$. The individual relative abundances of the ions $[M + H - C_6(H,D)_6]^+$ formed from (**5a**), (**6**), and (**5b**) fit clearly between these two extremes. For the open-chain diphenylalkanes, the rates (k_H) of the interannular proton transfer in $[M + H]^+$ ions that fragment in the *second* field-free region have been estimated by kinetic model calculations to be k_H *ca.* 5×10^5 s^{-1} {[(**1**) + H]$^+$} and $k_H \geq 1 \times 10^6$ s^{-1} {[(**2**) + H]$^+$}.[2,4] Therefore, from the comparison of the peak pattern obtained for the $[M + H]^+$ ions which decompose in the *first* FFR of the mass spectrometer (Table, entries B/E), the rates for the interannular proton transfer in metastable ions [(**5b**) + H]$^+$ and [(**6**) + H]$^+$ which fragment in the second FFR are estimated to lie within the limits $5.10^5 \leq k_H \leq 10^6$ s^{-1}.

Stereocontrol affects the extent of proton equilibration in the same way as does ion lifetime, as shown by the fragmentation of [(**5b**) + H]$^+$ in two field-free regions of the mass spectrometer. In particular, the kinetic model calculations[2,4,5] revealed that the losses of C_6H_5D and $C_6H_2D_4$ exhibit relative maxima with an increasing number of proton exchange steps (*i.e.* increasing ion lifetime). The loss of benzene isotopomers from ions [(**5b**) + H]$^+$ fragmenting in the second field-free region (*i.e.* longer ion lifetimes) is closer to the statistical pattern than that of ions fragmenting in the first field-free region (*i.e.* shorter ion lifetime). The same effect has now been demonstrated by varying the rate of interannular proton transfer by the stereocontrolling influence of the cyclohexane-1,4-diyl unit in protonated (**5a**), (**5b**), and (**6**).

Experimental

Mass Spectrometry.—Mass spectrometry was carried out using a double focusing instrument (ZAB-2F, V.G. Analytical Ltd., Manchester, UK), the electric sector following the magnetic one. CI source conditions: electron energy 100 eV, emission current 200 μA, accelerating voltage 5.6 kV, temperature 160–180 °C, reactant gas isobutane (Matheson, stated purity ≥99.5%), nominal pressure 8×10^{-4} to 2.5×10^{-3} Pa. Hydrocarbons (**5a**), (**5b**), and (**6**) were introduced with the air-cooled direct inlet probe; the data given in the Table are average values from several independent series of at least eight scans. B/E scans were recorded with the intermediate and the exit slits closed such that the intensity ratio $[M + H]^+/[M]^{+\bullet}$ was $\geq 10^4$.

Materials.—The synthesis of the hydrocarbons (**5a**), (**5b**), and (**6**) is outlined in Scheme 2. Dibromides (**7a**) and (**7b**) were synthesized in accord with the literature.[11–13] M.p.s were determined with an Electrothermal melting point apparatus and are uncorrected.

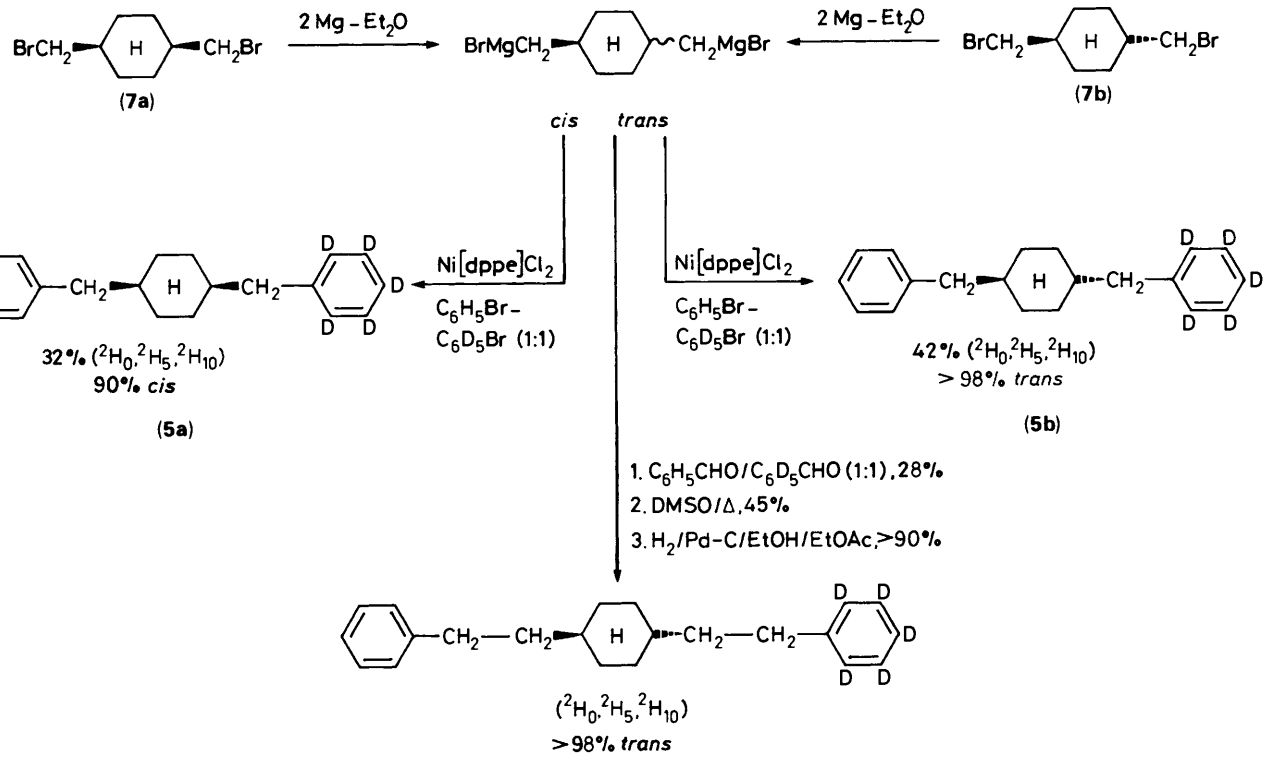
cis-1,4-*Bis(hydroxymethyl)-cyclohexane*[11] was obtained by catalytic hydrogenation of terephthalic acid followed by $LiAlH_4$ reduction. Analysis of the ^1H NMR spectrum showed the presence of *ca.* 10% of the *trans* isomer, due to the low selectivity of the first step. Colourless oil (b.p. 200 °C at 13 Pa, Kugelrohr); δ_H(300 MHz, $CDCl_3$; $SiMe_4$): 1.26–1.75 (m, 12 H) and 3.55 (d, 4 H, J 6.5 Hz); MS (EI, 70 eV) m/z 126, ([$M - H_2O$]$^{+\bullet}$, 5%), 114 (5), 108 (25), 96 (33), 95 (100), 93 (37), 81 (25), 80 (13), 79 (23), 69 (14), 67 (53), 57 (13), 55 (34), 41 (38), and 31 (20).

trans-1,4-*Bis(hydroxymethyl)cyclohexane*[11] was synthesized by reduction of dimethyl *trans*-cyclohexane-1,4-dicarboxylate,[11] which was obtained by esterification of the corresponding diacid (Aldrich, purity 99%) with $LiAlH_4$. Colourless crystals (m.p. 65.5–66.5 °C); δ_H(60 MHz; $CDCl_3$; $SiMe_4$) 0.7–2.0 (m, 12 H) and 3.47 (d, 4 H, J 6 Hz); MS (EI, 70 eV) m/z 126, ([$M - H_2O$]$^{+\bullet}$, 5%), 113 (4), 108 (24), 96 (8), 95 (100), 93 (25), 81 (7), 80 (8), 79 (13), 69 (10), 67 (30), 57 (7), 55 (18), 41 (23), and 31 (12).

cis-1,4-*Bis(bromomethyl)cyclohexane* (**7a**)[12] was prepared from the corresponding alcohol with PBr_3–benzene and contained *ca.* 10% of the *trans* isomer (**7b**) (see above), as shown by ^1H NMR spectroscopy. Colourless oil (b.p. 110 °C at 3 Pa, Kugelrohr); δ_H(300 MHz, $CDCl_3$; $SiMe_4$) 1.45–1.67 (m, 8 H), 1.85–1.90 (m, 2 H), and 3.38 (d, 4 H, J 7.1 Hz). MS (EI, 70 eV) and m/z 189/191 ([M – Br]$^+$, 19/16), 188/190 (2/3), 135 (2), 109 (100), 95 (53), 81 (6), 67 (36), 55 (27), 53 (12), 41 (32), and 39 (15); the spectrum depends strongly on the temperature of the direct inlet rod.

trans-1,4-*Bis(bromomethyl)cyclohexane* (**7b**)[13] was prepared from the *trans*-diol with PBr_3–benzene, analogously with the *cis*-isomer preparation. The product was purified by distillation through a small Vigreux column (b.p. 80–83 °C at 3 Pa), followed by recrystallization from methanol–diethyl ether (× 3) to give, colourless, leafy crystals (m.p. 54.5–55.5 °C) (55%). δ_H(300 MHz; $CDCl_3$; $SiMe_4$) 1.07 (m, 4 H), 1.61 (m, 2 H), 1.94 (m, 4 H), and 3.29 (d, 4 H, J 6.2 Hz); ν(KBr) 2 910, 2 840, 1 450, 1 380, 1 345, 1 300, 1 270, 1 205, 945, 910, 640, and 560 cm^{-1}; MS (EI, 70 eV) m/z 270, ([^{79}Br, ^{81}Br] – $M^{+\bullet}$, 0.07%), 188/190 (11/11), 109 (100), 95 (60), 81 (8), 67 (32), 55 (31), 53 (14), 41 (33), and 39 (22). Compound (**7b**) can also be obtained by reaction of the diol mixture and fractionated recrystallization of the crude (**7a, b**) mixture.

The cis- *and* trans-1,4-*Dibenzylcyclohexanes* (**5a**) and (**5b**) were synthesized by reaction of the bis-(Grignard) derivatives of (**7a**) and (**7b**), respectively, with a 1 : 1 mixture of bromobenzene and [$^2H_5$]bromobenzene (isotopic purity of C_6D_5Br 99%,



Scheme 2.

Merck) in the presence of (diphenylphosphinoethane) nickel(II) chloride, Ni(dppe)Cl_2.[14] The procedure is described in detail for the unlabelled *trans* isomer (**5b**).

trans-1,4-*Dibenzylcyclohexane* (**5b**). Dibromide (**7b**) (2.7 g, 10 mmol), dissolved in dry diethyl ether (12 cm^3), was added in the usual manner to magnesium turnings (490 mg, 20 mmol) and diethyl ether (3 cm^3) under N_2. The slightly exothermic reaction was completed by heating to reflux for 30 min. The reaction mixture, consisting of two liquid phases (a heavier, grey and a lighter, colourless phase) was cooled to 0 °C and dropped into a stirred solution of bromobenzene (3.14 g, 20 mmol) in dry ether (10 m^3), containing Ni(dppe)Cl_2 (70 mg, 0.13 mmol), at 0 °C over 10 min. During this time the catalyst dissolved, and the solution turned green and then black. After being heated to reflux for 17 h, the mixture was cooled, hydrolysed with HCl (2 mol dm^{-3}), and extracted with diethyl ether. The combined ether layers were washed (water) and dried (Na_2SO_4). After removal of the solvent under reduced pressure, the oily residue was purified by Kugelrohr distillation. The fractions obtained in the range 100–200 °C at 3 Pa were combined and recrystallized from methanol containing a small amount of diethyl ether, to give colourless crystals (1.1 g), which were shown, by TLC (silica gel, light petroleum–diethyl ether, 10:1), to be slightly contaminated. Two further recrystallizations furnished pure (**5b**) in 42% yield, m.p. 87–87.5 °C. δ_H(300 MHz; $CDCl_3$; $SiMe_4$) 0.92 (m, 4 H), 1.47 (m, 2 H), 1.68 (m, 4 H), 2.46 (m, 4 H, *J* 7.0 Hz), and 7.1–7.27 (m, 10 H); ν(KBr) 3 080, 3 055, 3 020, 2 900, 2 830, 1 595, 1 485, 1 440, 1 275, 1 080, 1 055, 1 025, 905, 740, 695, 580, and 460 cm^{-1}; MS (EI, 70 eV) *m/z* 264, ($M^{+\cdot}$, 11%), 173 (12), 172 (5), 117 (4), 105 (9), 95 (6), 91 (100), 81 (14), 80 (9), 65 (6), and 41 (6). (Found: C 90.59, H 9.52. Calc. C 90.85, H 9.15%).

cis-1-*Benzyl*-4-([2,3,4,5,6-$^2H_5$]*benzyl*)*cyclohexane* (**5a**). This compound was synthesized in a similar manner to the procedure given above from (**7a**) (1.3 g, 4.8 mmol), containing *ca.* 10% of the *trans* isomer (**9b**), and a solution prepared from C_6H_5Br and C_6D_5Br (each 4.8 mmol) and Mg (9.6 mmol). The compound was obtained as colourless crystals, m.p. 45–46.5 °C (32%) after recrystallisation from methanol–diethyl ether (× 3). On the basis of the ^1H NMR spectrum, the impurity [*ca.* 10% (**5b**)] was assumed not to be removable by this procedure. The mass spectrum confirmed the expected 1:2:1 mixture of [$^2H_0$], [$^2H_5$], and [$^2H_{10}$] isotopomers. δ_H(300 MHz; $CDCl_3$; $SiMe_4$) 1.43 (m, 8 H), 1.76 (m, 2 H), 2.60 (d, 4 H, *J* 6.6 Hz), and 7.10–7.27 (m, 5 H); MS (EI, 70 eV) *m/z* 274, ([$^2H_{10}$] − $M^{+\cdot}$, 10.3), 269, ([$^2H_5$] − $M^{+\cdot}$, 22.6), 264, ([$^2H_0$] − $M^{+\cdot}$, 11.6), 178 (15), 177 (6), 173 (16), 172 (6), 110 (5), 105 (9), 96 (76), 95 (30), 91 (100), 81 (31), and 80 (23).

trans-1-*Benzyl*-4-([2,3,4,5,6-$^2H_5$]*benzyl*)*cyclohexane* (**5b**). This compound was synthesized on the same scale as isomer (**5a**) and obtained pure after two recrystallizations in 34% yield, m.p. 84.5–86 °C. δ_H(300 MHz; $CDCl_3$; $SiMe_4$) 0.92 (m, 4 H), 1.48 (m, 2 H), 1.68 (m, 4 H), 2.46 (d, 4 H, *J* 7.0 Hz), and 7.1–7.27 (m, 10 H); MS (EI, 70 eV) *m/z* 274, ([$^2H_{10}$] − $M^{+\cdot}$, 9.3), 269, ([$^2H_5$] − $M^{+\cdot}$, 20.6), 264, ([$^2H_0$] − $M^{+\cdot}$, 11.5), 178 (16), 177 (4), 173 (18), 172 (6), 110 (5), 105 (10), 96 (72), 95 (26), 91 (100), 81 (28), and 80 (19).

trans-1-(2-*Hydroxy*-2-*phenylethyl*)-4-[(2-*hydroxy*-2-[$^2H_5$]-*phenyl*)*ethyl*]*cyclohexane*. The bis-(Grignard) derivative was prepared under N_2 from *trans* dibromide (**7b**) (2.16 g, 8 mmol) as described above. A solution of [$^2H_0$]benzaldehyde (0.85 g, 8 mmol) and [$^2H_5$]benzaldehyde (0.89 g, 8 mmol) was dropped into the Grignard reagent. In spite of vigorous stirring, the reaction mixture formed a viscous mass, which was dissolved in dry tetrahydrofuran (20 cm^3). The solution was heated to reflux for 2 h, cooled, and hydrolysed with ice (3 g). Aqueous NH_4Cl was added which just allowed the solid components to dissolve. After extraction with diethyl ether, the combined extracts were washed (aqueous $NaHCO_3$ and water), dried ($MgSO_4$), and concentrated under reduced pressure to give a yellow oil. Recrystallization from light petroleum–diethyl ether gave

colourless crystals, m.p. 125–130 °C, (28%), which consisted, by TLC [silica gel, light petroleum–diethyl ether (9:1)], of two diastereoisomers. δ_H(300 MHz; $CDCl_3$; $SiMe_4$) 0.96 (m, 4 H), 1.37 (m, 2 H), 1.45–1.57 (m, 4 H), 1.67–1.87 (m, 6 H), 4.78 (m, 2 H), and 7.25–7.35 (m, 5 H); MS (EI, 70 eV) *m/z* 316 $[([^2H_{10}]M - H_2O)^{+\bullet}$, 1.8], 311 $[([^2H_5]M - H_2O)^{+\bullet}$, 2.6], 306 $[([^2H_0]M - H_2O)^{+\bullet}$, 1.0], 298 $[([^2H_{10}]M - 2H_2O)^{+\bullet}$, 1.5], 293 $[([D_5]M - 2H_2O)^{+\bullet}$, 2.4], 288 $[([^2H_0]M - 2H_2O)^{+\bullet}$, 1.0], 205 (35), 200 (25), 112 (100), 109, (63), 107 (75), 104 (37), 96 (18), 95 (17), 91 (10), 84 (45), and 79 (37).

trans-1-*Styryl*-4-([2,3,4,5,6-$^2H_5$]*styryl*)*cyclohexane*. The diol (500 mg, 1.5 mmol) was dissolved in DMSO (1.5 g, freshly distilled from CaH_2) under N_2 and heated to 170 °C for 20 h. The reaction mixture was cooled, diluted with water, extracted with light petroleum–diethyl ether (40:70), and the insoluble residue of the mixture was separated. The organic extracts (including the ethereal solution from the insoluble residue) were combined, washed with water (×3), dried ($MgSO_4$), and solvent was removed by evaporation. The resulting oil was recrystallized from methanol–diethyl ether to yield yellow-brown crystals (200 mg). Micro column chromatography [silica gel, light petroleum–diethyl ether (40:70)] followed by another recrystallization from methanol–diethyl ether gave almost colourless, voluminous crystals, m.p. 151–156 °C, (45%). δ_H(300 MHz; $CDCl_3$; $SiMe_4$) 1.29 (m, 4 H), 1.91 (m, 4 H), 2.11 (m, 2 H), 6.19 (dd, 2 H *J* 15.9, 6.8 Hz) 6.38 (d, 2 H, *J* 15.9 Hz), and 7.19–7.37 (m, 5 H); MS (EI, 70 eV) *m/z* 298, $([^2H_{10}] - M^{+\bullet}$, 76.2), 293, $([^2H_5] - M^{+\bullet}$, 100), 288, $([^2H_0] - M^{+\bullet}$, 34.2), 202 (15), 197 (13), 188 (31), 183 (37), 174 (17), 169 (14), 161 (30), 156 (21), 134 (43), 129 (41), 96 (46), and 91 (49). The ^1H NMR data point to a *trans* configuration of the double bonds.

trans-1-(2-*Phenylethyl*)-4-(2-[$^2H_5$]*phenylethyl*)*cyclohexane* (**6**). The alkene (120 mg, 0.41 mmol) was dissolved in ethanol (5 cm^3) and ethyl acetate (7 cm^3) and hydrogenated at room temperature and atmospheric pressure in the presence of Pd/C (30 mg, 10%). Following removal of the catalyst and solvent the product was recrystallized from methanol–diethyl ether, to yield colourless crystals (80 mg; 90%), m.p. 79.5–81 °C. δ(300 MHz, $CDCl_3$; $SiMe_4$) 0.94 (m, 4 H), 1.22 (m, 2 H), 1.50 (m, 4 H *AA'XX'*) 1.81 (m, 4 H), 2.61 (m, 4 H *AA'XX'*), and 7.16–7.30 (m, 5 H) MS (EI, 70 eV) *m/z* 302, $([^2H_{10}] - M^{+\bullet}$, 11.6), 297, $([^2H_5] - M^{+\bullet}$, 16.0), 292, $[^2H_o] - M^{+\bullet}$, 5.5), 206 (1.7), 205 (1.5), 201 (1.1), 200 (1.3), 97 (100), 96 (42), 92 (71), and 91 (32).

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