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Skeletal Rearrangement for Water Loss from Molecular Protonated Ions of *t*-Butoxycyclohexane

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Isotopic labelling and chemical substitution support the proposition that the skeletal rearrangement for water loss from molecular protonated ions of *t*-butoxycyclohexane involves competition between three reaction pathways. The principal reaction pathway (83%) involves migration of the *t*-butyl group to the 2-(6-) position of the cyclohexyl ring with reciprocal hydrogen transfer. A second reaction pathway (12%) involves ring contraction followed by reciprocal exchange of the *t*-butyl group with the 2-(5-) hydrogen atom of the nascent cyclopentyl ring. The third reaction pathway (5%) involves rearrangement of a proton-bound complex to permit *ipso* attack by isobutene. Stereospecific substitutions indicate that the principal reaction pathway is susceptible to 1,3-diaxial interactions.

INTRODUCTION

Gaseous even-electron ions generally have a greater propensity for rearrangement than odd-electron ions[1] and merit broad interest because of correlations of their structure/activity relationships with those of analogous ions in solution. Representative hydrogen and skeletal rearrangements of molecular protonated ions (MH^+) generated under chemical ionization (CI) conditions have been reviewed.[2] Following an earlier communication reporting the occurrence of skeletal rearrangements of MH^+ ions of some open-chain ethers,[3] we have since elucidated the mechanisms of such rearrangements in the CI mass spectra of dibenzyl ether[4] and benzyl 2-phenylethyl ether.[5]

We noted in particular that water loss occurs from MH^+ ions of alkoxycyclohexanes $C_6H_{11}OR$ when R is allyl, benzyl or *t*-butyl but does not occur either in the ion chamber or the flight path when R is methyl, ethyl or phenyl.[3] The present investigation was initiated to clarify the skeletal rearrangement for dehydration under CI conditions of MH^+ ions of *t*-butoxycyclohexane.

RESULTS AND DISCUSSION

General considerations

While water loss does not occur from MH^+ ions of *t*-butoxycyclopropane[6] or *t*-butoxyethane[7] under CI(CH_4) conditions, the present study shows that the particular structural requirements for the skeletal rearrangement are available with *t*-butoxycyclohexane. This rearrangement takes place under CI(H_2) and CI(iso-C_4H_{10}) conditions both in the ion chamber and the flight path (first field-free region (1st FFR) AEI MS902).

As a preliminary consideration of possible mechanisms for water loss from MH^+ ions of *t*-butoxycyclohexane, it is relevant to note that water loss also occurs readily from the isomeric $[M + C_4H_9]^+$ ions formed in the CI(iso-C_4H_{10}) mass spectrum of cyclohexanol[8] and from ephemeral MH^+ ions formed in the CI(iso-C_4H_{10}) mass spectra of various *t*-butylcyclohexanols.[9] Isotopic labelling of the various sites of *t*-butoxycyclohexane and of the reagent proton have been carried out in order to elucidate the source of hydrogen atoms incorporated in the water loss.

Because interpretations of ion source reactions can be confused by competing pathways to the daughter ions of interest, the parents and progeny for the labelled compounds were specified by selecting reactions occurring in the 1st FFR. This strategy has the additional advantages of permitting a constant time frame for widely different reagent plasmas and of circumventing problems due to possible intermolecular exchange reactions of daughter ions within the ion chamber.

Hydrogen atoms involved in the water loss

The labelling results for water loss from MH^+ ions of *t*-butoxycyclohexane are shown in Table 1.

It is evident that cyclohexyl-ring hydrogen atoms are involved regioselectively in the reaction and that the principal sources of hydrogen in the water loss are the 2-(6-) position and the *t*-butyl group. In contrast to results for dibenzyl ether,[4] the reagent proton is hardly involved in the reaction, indicating that its positional identity has been compromised by its far more extensive dilution with other hydrogen atoms in the molecule.

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Table 1. Observed isotopic distributions for water loss from MH^+ ions of *t*-butoxycyclohexane (1st FFR)

Substrate labelling	Reagent plasma	Relative proportions H_2O	HOD	D_2O
2,2,6,6-$^2H_4$	H_2	0.16	0.84	0.00
	C_4H_{10}	0.12	0.88	0.00
3,3,5,5-$^2H_4$	H_2	0.96	0.04	0.00
	C_4H_{10}	0.96	0.04	0.00
4,4-$^2H_2$	H_2	0.99	0.01	0.00
	C_4H_{10}	0.99	0.01	0.00
1-$^2H_1$	H_2	0.98	0.02	0.00
	C_4H_{10}	0.98	0.02	0.00
cyclohexyl-$^2H_{11}$	H_2	0.08	0.92	0.00
	C_4H_{10}	0.06	0.94	0.00
t-butyl-$^2H_9$	H_2	0.12	0.85	0.03
	C_4H_{10}	0.12	0.88	0.00
unlabelled	D_2/D_2O	0.92	0.08	0.00
t-butyl-$^2H_9$	D_2/D_2O	0.04	0.92	0.04

Thus, it is clear that a single mechanism would be insufficient to accommodate the observed isotopic distributions and that any model to simulate the distributions has to account, *inter alia*, for the following observations:

(i) H_2O loss from 2,2,6,6-$^2H_4$ ether;
(ii) HOD loss from 3,3,5,5-$^2H_4$ ether;
(iii) D_2O loss from *t*-butyl-$^2H_9$ ether;
(iv) H_2O loss from cyclohexyl-$^2H_{11}$ ether.

Simulation of isotopic distributions

A number of assumptions [(a)–(d)] have been made in order to simulate the isotopic distributions for water loss from MH^+ ions of *t*-butoxycyclohexane.

(a) All MH^+ ions surviving until the 1st FFR are initially oxygen-protonated and one of the hydrogen atoms of the eliminated water arises from the randomized pool of the reagent proton and the *t*-butyl group.

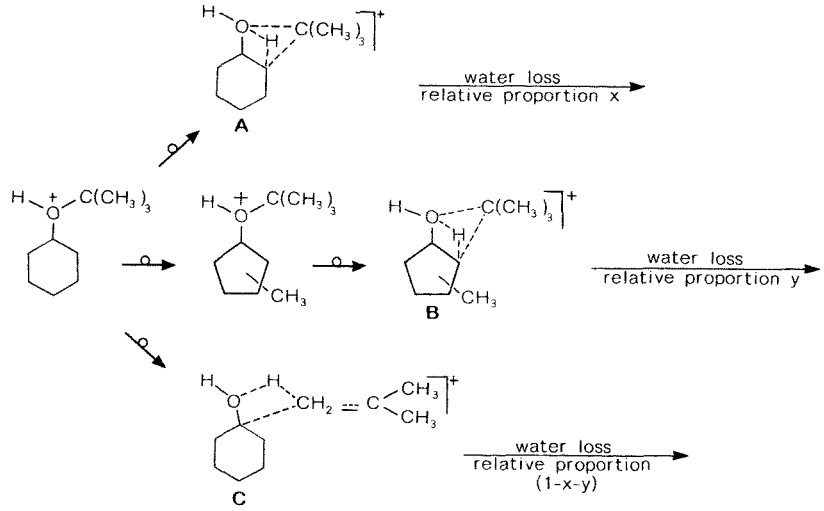
(b) Three reaction intermediates (Scheme 1) are in competition for the skeletal rearrangement. Intermediate A involves reciprocal exchange of the *t*-butyl group with the 2-(6-) hydrogen atom of the cyclohexyl ring. Intermediate B is preceded by ring contraction and involves reciprocal exchange of the *t*-butyl group with the 2-(5-) hydrogen atom of the nascent cyclopentyl ring. In this regard, we find that water loss is an important fragmentation of MH^+ ions of *t*-butoxycyclopentane. Intermediate C involves a proton-bound complex somewhat analogous to that suggested to explain results for loss of water from $[M + C_4H_9]^+$ ions of benzyl alcohol.[10]

(c) The positional integrity of the ring labels is maintained before the alkyl migration step for the reaction pathway that proceeds through intermediate A. In contrast, the ring hydrogen atoms have completely lost their positional identity after ring contraction and therefore, for the reaction pathway that proceeds through intermediate B, the erstwhile cyclohexyl hydrogen atoms are considered to be equally available for reciprocal exchange with the *t*-butyl group. Ring contractions have been proposed previously for a number of gaseous even-electron cyclohexyl ions.[2] For instance, persuasive evidence has been presented to demonstrate that a ring contraction precedes water loss from MH^+ ions of 2,2,6,6-tetramethylcyclohexanone.[11]

(d) Primary kinetic isotope effects are negligible for the water loss. This is consistent with the nature of the suggested reaction intermediates (Scheme 1), but contrasts with the results of our simulations of the labelling data for water loss from dibenzyl ether[4] and benzyl 2-phenylethyl ether[5] where the proposed rate-determining steps for the fragmentations were hydrogen transfers.

Let x and y be the proportions of water loss involving intermediates A and B, respectively. It can be readily shown that the relative losses of $H_2O:HOD:D_2O$ from the various labelled derivatives of *t*-butoxycyclohexane can be expressed in algebraic terms as in Table 2, assuming propositions (a)–(d) to be valid.

Iterative calculations indicate that a best fit to the



Scheme 1. Model for competitive pathways to water loss from MH^+ ions of *t*-butoxycyclohexane.

Table 2. Expressions for isotopic distributions for water loss from MH^+ ions of *t*-butoxycyclohexane, where *x* and *y* are proportions of reaction involving intermediates A and B, respectively

Substrate	Plasma	Relative proportions H_2O	HOD	D_2O
2,2,6,6-$^2H_4$	H^+	$(1-x-0.36y)$	$(x+0.36y)$	0
3,3,5,5-$^2H_4$	H^+	$(1-0.36y)$	$0.36y$	0
4,4-$^2H_2$	H^+	$(1-0.18y)$	$0.18y$	0
1-$^2H_1$	H^+	$(1-0.09y)$	$0.09y$	0
cyclohexyl-$^2H_{11}$	H^+	$(1-x-y)$	$(x+y)$	0
t-butyl-$^2H_9$	H^+	$0.1(x+y)$	$0.7(x+y)+0.2$	$0.8(1-x-y)$
unlabelled	D^+	$0.1(x+y)+0.8$	$0.2-0.1(x+y)$	0
t-butyl-$^2H_9$	D^+	0	$(x+y)$	$(1-x-y)$

observed isotopic distributions is obtained when the relative proportions of water loss involving intermediates A, B and C are 83%, 12% and 5%, respectively. The calculated and observed distributions for the losses of isotopomers from the various labelled derivatives are shown in Table 3. There is good agreement between the distributions, which lends support to the validity of the proposed model. The minor peak observed for H_2O loss from MD^+ ions of *t*-butoxy-$^2H_9$-cyclohexane is unexpected on the basis of the proposed model but may be due to interference from CD_3 loss.

An alternative alkyl rearrangement

A plausible alternative to the principal alkyl rearrangement for *t*-butoxycyclohexane (A, Scheme 1) that is consistent with the labelling results (Table 1) can be proposed. This involves reciprocal migration of the *t*-butyl group to the 4-position of the cyclohexyl ring and a 1,3-hydrogen shift from the 2-(6-) position to the oxygen atom.[3] Such a reaction implies ring cleavage and its relative importance in the competing pathways (Scheme 1) would be susceptible to steric and electronic effects of alkyl substituents in the 3-, 4- and 5- positions of the ring.

Our present results do not support the suggestion that *t*-butyl migration to the 4-position occurs alternatively or competitively to the proposed rearrangement to the 2-position. The regioselectivity of hydrogen migration from the 2-(6-) position is quite insensitive to the alkyl substitution. Thus, for 2,2,6,6-$^2H_4$ labelling and alkyl substituents *cis*/*trans*-4-methyl, *cis*/*trans*-4-*t*-butyl, 4,4-dimethyl, 3,3-dimethyl and 3,3,5,5-tetramethyl, the observed relative proportions of losses of $H_2O:HOD:D_2O$ are $(0.15 \pm 0.03):(0.85 \pm 0.03):0.00$, practically the same as for the unsubstituted ether (Table 1).

Table 3. Isotopic distributions for water loss from MH^+ ions of *t*-butoxycyclohexane where relative proportions of the reaction involving intermediates A, B and C are 83%, 12% and 5%, respectively

Substrate	Plasma	Calculated relative proportions H_2O	HOD	D_2O	Observed relative proportions[a] H_2O	HOD	D_2O
2,2,6,6-$^2H_4$	H^+	0.13	0.87	0.00	0.14	0.86	0.00
3,3,5,5-$^2H_4$	H^+	0.96	0.04	0.00	0.96	0.04	0.00
4,4-$^2H_2$	H^+	0.98	0.02	0.00	0.99	0.01	0.00
1-$^2H_1$	H^+	0.99	0.01	0.00	0.98	0.02	0.00
cyclohexyl-$^2H_{11}$	H^+	0.05	0.95	0.00	0.07	0.93	0.00
t-butyl-$^2H_9$	H^+	0.10	0.86	0.04	0.12	0.86	0.02
unlabelled	D^+	0.90	0.10	0.00	0.92	0.08	0.00
t-butyl-$^2H_9$	D^+	0.00	0.95	0.05	0.04	0.92	0.04

[a] Mean ratios, 1st FFR fragmentations.

Stereochemical effects

The results of stereoisomeric substitutions in the 3- and 5- positions of the cyclohexyl ring are given in Table 4. There is a larger proportion of H_2O lost from MH^+ ions of the labelled *cis*-substituted isomers than from the *trans*-substituted isomers. Molecular models show that the *cis*-3-substituted isomers are subjected to significant 1,3-diaxial interactions when the *t*-butoxy group is axial. For this conformation, therefore, the proportion of HOD lost from the 2,2,6,6-$^2H_4$ ethers is expected to be depressed, which is observed. The effect is particularly striking for the isomeric 3-*t*-butyl and 3,3,5-trimethyl derivatives (Table 4). The inferences from these results are that the principal rearrangement *via* intermediate A proceeds only when the *t*-butoxy group is *axial* and that, although steric hindrance is minimal when the *t*-butoxy group is *equatorial*, water loss for

Table 4. Observed isotopic distributions for water loss from MH^+ ions of alkyl-substituted *t*-butoxycyclohexane-2,2,6,6-$^2H_4$ (1st FFR)

Substrate	Reagent plasma	Relative proportions H_2O	HOD	D_2O
cis-3-methyl	H_2	0.21	0.79	0.00
	C_4H_{10}	0.16	0.84	0.00
trans-3-methyl	H_2	0.16	0.84	0.00
	C_4H_{10}	0.17	0.83	0.00
cis-3-*t*-butyl	H_2	0.29	0.71	0.00
	C_4H_{10}	0.28	0.72	0.00
trans-3-*t*-butyl	H_2	0.12	0.88	0.00
	C_4H_{10}	0.10	0.90	0.00
cis-3,3,5-trimethyl	H_2	0.28	0.72	0.00
	C_4H_{10}	0.22	0.78	0.00
trans-3,3,5-trimethyl	H_2	0.10	0.86	0.04
	C_4H_{10}	0.09	0.89	0.02

this latter conformation is pre-empted by alternative fragmentations.

When a *t*-butyl group is introduced into the 2-position of the cyclohexyl ring, water loss is completely (*cis*-isomer) or substantially (*trans*-isomer) suppressed. Molecular models show that, when the *t*-butoxy group is *axial* for both isomers, the substituent *t*-butyl group sterically hinders the rearrangements for water loss by way of all intermediates.

EXPERIMENTAL

CI mass spectra were obtained by direct insertion on an AEI MS902 mass spectrometer fitted with a CIS2 ion source, using procedures similar to those described previously.[4,5,12]

Relative peak heights for daughter ions resulting from fragmentations in the 1st FFR (FFR between the ion source and electric sector) were obtained through linked microprocessor control of the electric sector voltage and magnetic field,[13] and are averaged values of at least three scans. Labelling of the reagent proton was achieved through the use of D_2 gas containing a small proportion of D_2O.[4,5,12]

All compounds except the α-deuterated ketones were purified by preparative gas chromatography prior to mass spectrometry, using procedures described previously.[4,5,12] NMR spectra were obtained either on a Varian A60, a Jeol JNM-4H-100 or a Jeol FX 100 spectrometer. Elemental analyses were carried out by Mr J. Sussman and Dr P. Phung of the University of New South Wales. The molecular identity and homogeneity of the unlabelled compounds were validated by mass spectrometry (electron ionization, 70 eV). Deuterium incorporation for the labelled compounds was assessed by mass spectrometry (electron ionization, 12–15 eV) to be generally greater than 95 atom % D.

t-Butoxycyclohexane was prepared from cyclohexanol and isobutene using a published procedure.[14]

t-Butoxycyclohexane-$^2H_{11}$ was prepared similarly from cyclohexanol-$^2H_{11}$.

t-Butoxycyclohexane-1-$^2H_1$ was prepared similarly from cyclohexanol-1-$^2H_1$.[12]

t-Butoxycyclohexane-2,2,6,6-$^2H_4$ was prepared similarly from cyclohexanol-2,2,6,6-$^2H_4$.[15]

t-Butoxycyclohexane-3,3,5,5-$^2H_4$ was prepared from 4-*t*-butoxycyclohexanone-2,2,6,6-$^2H_4$[12] by reduction of the ketone with lithium aluminium hydride using the general method described by Klein and Smith.[15]

t-Butoxycyclohexane-4,4-$^2H_2$ was prepared from 4-*t*-butoxycyclohexanone[12] by reduction of the ketone with lithium aluminium deuteride using the general procedure of Klein and Smith.[15]

t-Butoxy-$^2H_9$-cyclohexane was prepared from *t*-butyl-$^2H_9$ alcohol and cyclohexene using a published procedure.[16]

In general, the alkyl-substituted *t*-butoxycyclohexanes were synthesized by reaction of isobutene with the appropriate unlabelled or labelled alcohol.

cis-3-Methylcyclohexanol-2,2,6,6-$^2H_4$ was prepared from 3-methylcyclohexanone by deuterium exchange[17] followed by reduction.[18]

trans-3-Methylcyclohexanol-2,2,6,6-$^2H_4$ was prepared from 3-methylcyclohexanone by deuterium exchange[17] followed by reduction.[19]

cis/trans-4-Methylcyclohexanol-2,2,6,6-$^2H_4$ were synthesized by analogous procedures.

cis-3-*t*-Butylcyclohexanol-2,2,6,6-$^2H_4$ was prepared by deuterium exchange[17] followed by reduction[18] of 3-*t*-butylcyclohexanone, which had been synthesized previously by chromic acid oxidation[20] of 3-*t*-butylcyclohexanol.[21]

trans-3-*t*-Butylcyclohexanol-2,2,6,6-$^2H_4$ was prepared by deuterium exchange[17] and reduction[22] of 3-*t*-butylcyclohexanone.

cis/trans-4-*t*-Butylcyclohexanol-2,2,6,6-$^2H_4$ were synthesized by analogous procedures.

3,3-Dimethylcyclohexanol-2,2,6,6-$^2H_4$ was prepared by deuterium exchange followed by reduction of 3,3-dimethylcyclohexanone.

4,4-Dimethylcyclohexanol-2,2,6,6-$^2H_4$ was prepared from 4,4-dimethylcyclohexanol by chromic acid oxidation, deuterium exchange and reduction.

cis/trans-3,3,5-Trimethylcyclohexanol-2,2,6,6-$^2H_4$ were prepared from 3,3,5-trimethylcyclohexanone by deuterium exchange[17] followed by stereoselective reduction.[23]

3,3,5,5-Tetramethylcyclohexanol-2,2,6,6-$^2H_4$ was prepared from 3,3,5,5-tetramethylcyclohexanone[24] by deuterium exchange followed by reduction.

cis-*t*-Butoxy-3-methylcyclohexane was prepared as a colourless liquid by the reaction of *cis*-3-methylcyclohexanol[18] with isobutene. (Found: C, 77.7; H, 12.8. Calc. for $C_{11}H_{22}O$: C, 77.6; H, 13.0%). NMR ($CDCl_3$): 0.89 (d, 3H, CH–C$\underline{H}_3$); 1.18 (s, 9H, C(C$\underline{H}_3$)$_3$); 1.43 (m, 9H, ring C$\underline{H}_2$, C–C$\underline{H}$); 3.33 (m, 1H, O–C$\underline{H}$).

trans-*t*-Butoxy-3-methylcyclohexane was prepared similarly from *trans*-3-methylcyclohexanol[19] as a colourless liquid. (Found: C, 77.5; H, 13.3. Calc. for $C_{11}H_{22}O$: C, 77.6; H, 13.0%). NMR ($CDCl_3$): 0.88 (d, 3H, CH–C$\underline{H}_3$); 1.15 (s, 9H, C(C$\underline{H}_3$)$_3$); 1.46 (m, 9H, ring C$\underline{H}_2$, C–C$\underline{H}$); 3.72 (m, 1H, O–C$\underline{H}$).

cis-*t*-Butoxy-3-*t*-butylcyclohexane was prepared similarly from *cis*-3-*t*-butylcyclohexanol. (Found: C, 79.1; H, 13.4. Calc. for $C_{14}H_{28}O$: C, 79.2; H, 13.3%). NMR ($CDCl_3$): 0.84 (s, 9H, C(C$\underline{H}_3$)$_3$); 1.19 (s, 9H, OC(C$\underline{H}_3$)$_3$); 1.74 (m, 9H, ring C$\underline{H}_2$, C–C$\underline{H}$); 3.31 (s, 1H, OC$\underline{H}$).

trans-*t*-Butoxy-3-*t*-butylcyclohexane was prepared similarly from *trans*-3-*t*-butylcyclohexanol. (Found: C, 79.5; H, 13.5. Calc. for $C_{14}H_{28}O$: C, 79.2; H, 13.3%). NMR ($CDCl_3$): 0.82 (s, 9H, C(C$\underline{H}_3$)$_3$); 1.19 (s, 9H, OC(C$\underline{H}_3$)$_3$); 1.74 (m, 9H, ring C$\underline{H}_2$, C–C$\underline{H}$); 3.31 (s, 1H, OC$\underline{H}$).

cis-t-Butoxy-4-methylcyclohexane was prepared similarly from *cis*-4-methylcyclohexanol. NMR ($CDCl_3$): 0.91 (d, 3H, $CHC\underline{H}_3$); 1.16 (s, 9H, $C(C\underline{H}_3)_3$); 1.45 (m, 9H, ring $C\underline{H}_2$, C–C$\underline{H}$); 3.52 (m, 1H, OC$\underline{H}$).

trans-t-Butoxy-4-methylcyclohexane was prepared similarly from *trans*-4-methylcyclohexanol. NMR ($CDCl_3$): 0.86 (d, 3H, $CHC\underline{H}_3$); 1.18 (s, 9H, $C(C\underline{H}_3)_3$); 1.47 (m, 9H, ring $C\underline{H}_2$, C–C$\underline{H}$); 3.30 (m, 1H, OC$\underline{H}$).

t-Butoxy-3,3-dimethylcyclohexane was prepared similarly from 3,3-dimethylcyclohexanol. (Found: C, 78.2; H, 13.0. Calc. for $C_{12}H_{24}O$: C, 78.2; H, 13.1%). NMR ($CDCl_3$): 0.91 (s, 6H, $C(C\underline{H}_3)_2$); 1.17 (s, 9H, $C(C\underline{H}_3)_3$); 1.44 (m, 8H, ring $C\underline{H}_2$); 3.52 (m, 1H, OC$\underline{H}$).

t-Butoxy-4,4-dimethylcyclohexane was prepared similarly from 4,4-dimethylcyclohexanol.[25] (Found: C, 78.5, H, 13.3. Calc. for $C_{12}H_{24}O$: C, 78.2; H, 13.1%). NMR ($CDCl_3$): 0.89, 0.92 (2s, 6H, $2C\underline{H}_3$); 1.18 (s, 9H, $C(C\underline{H}_3)_3$); 1.46 (m, 8H, ring $C\underline{H}_2$); 3.29 (m, 1H, OC$\underline{H}$).

cis-t-Butoxy-3,3,5-trimethylcyclohexane was prepared similarly from *cis*-3,3,5-trimethylcyclohexanol.[23] (Found: C, 78.9; H, 13.0. Calc. for $C_{13}H_{26}O$: C, 78.7; H, 13.2%). NMR ($CDCl_3$): 0.84 (s, 3H, $C\underline{H}_3$); 1.18 (s, 9H, $C(C\underline{H}_3)_3$); 1.46 (m, 7H, ring $C\underline{H}_2$, C–C$\underline{H}$); 3.55 (m, 1H, O–C$\underline{H}$).

trans-t-Butoxy-3,3,5-trimethylcyclohexane was prepared similarly from *trans*-3-3,5-trimethylcyclohexanol.[23] (Found: C, 79.2; H, 13.8. Calc. for $C_{13}H_{26}O$: C, 78.7; H, 13.2%). NMR ($CDCl_3$): 0.84 (s, 3H, CH–$C\underline{H}_3$); 0.85 (d, 3H, CH–$C\underline{H}_3$); 1.06 (s, 3H, $C\underline{H}_3$); 1.13 (s, 9H, $C(C\underline{H}_3)_3$); 1.36 (m, 7H, ring $C\underline{H}_2$, C–C$\underline{H}$); 3.79 (m, 1H, OC$\underline{H}$).

t-Butoxy-3,3,5,5-tetramethylcyclohexane was prepared similarly from 3,3,5,5-tetramethylcyclohexanol.[24] (Found: C, 79.3; H, 13.4. Calc. for $C_{14}H_{28}O$: C, 79.2; H, 13.3%). NMR ($CDCl_3$): 0.89 (s, 6H, 2 × $C\underline{H}_3$); 1.03 (s, 6H, 2 × $C\underline{H}_3$); 1.19 (s, 9H, $C(C\underline{H}_3)_3$); 1.50 (m, 6H, ring $C\underline{H}_2$); 3.71 (m, 1H, OC$\underline{H}$).

cis-t-Butoxy-2-*t*-butylcyclohexane was prepared similarly from *cis*-2-*t*-butylcyclohexanol and purified by silica column chromatography prior to preparative gas chromatography. NMR ($CDCl_3$): 0.89 (s, 9H, $C(C\underline{H}_3)_3$); 1.21 (s, 9H, $OC(C\underline{H}_3)_3$); 1.52 (m, 9H, ring $C\underline{H}_2$, C–C$\underline{H}$); 4.02 (m, 1H, OC$\underline{H}$).

trans-t-Butoxy-2-*t*-butylcyclohexane was prepared similarly from *trans*-2-*t*-butylcyclohexanol and purified by silica column chromatography prior to preparative gas chromatography. NMR ($CDCl_3$): 0.97 (s, 9H, $C(C\underline{H}_3)_3$); 1.25 (s, 9H, $OC(C\underline{H}_3)_3$); 1.70 (m, 9H, ring $C\underline{H}_2$, C–C$\underline{H}$); 3.47 (m, 1H, OC$\underline{H}$).

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