Intermediate Formation of [4]Metacyclophane on Flash Vacuum Thermolysis

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Pyrolysis of 2,6-tetramethylene Dewar benzene (**2a**) under flash vacuum thermolysis (FVT) conditions at 400 °C gave 6- and 5-methylindan (**8a** (2.5%) and **10a** (2.5%), respectively) as well as tetralin (**5a**) (45%). These products indicate that [4]metacyclophane (**1a**) was formed in the gas phase, but it decomposed under the reaction conditions either via a homolytic cleavage of one of the benzylic bonds to yield a diradical (**6a**) leading to **8a** and **10a** or it gave **5a** via a benzvalene intermediate (**4a**). Deuterium labeling supports the proposed mechanism. A very similar course of events was observed on FVT of [5]metacyclophane at 600 °C; it yielded methyl-substituted tetralins (**8c**, **10c**) as the sole products. The analogies and differences in the behavior of the two metacyclophanes are discussed.

Since 1985 there has been a rapid development in the field of very short [*n*]cyclophanes.[1] In that year, the long sought [5]paracyclophane was synthesized in a photochemical reaction; it turned out to be thermally unstable above 0 °C.[2] Subsequently, slightly more stable derivatives were reported,[3] but it was so far impossible to prepare an isolable compound. The next lower homologue, [4]paracyclophane, could at first not be detected directly in photochemical or flash vacuum thermolysis (FVT) reactions,[4a] but irradiation of its Dewar isomer in the presence of acid yielded trapping products that provided chemical evidence for its intermediacy.[4b] Tsuji and Nishida presented direct UV spectroscopic evidence for [4]paracyclophane at low temperature.[5]

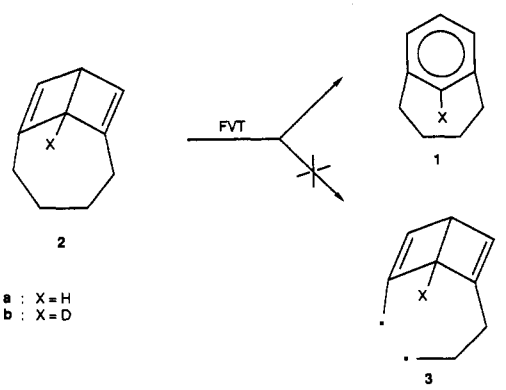
In the metacyclophanes series, the strain energy of a particular homologue is lower compared with that of its para isomer. Indeed, [5]metacyclophane (**1c**)[6] as well as several substituted derivatives[7] were known for some time and found to be reasonably stable inspite of the fact that in the case of the dichloro derivative an X-ray crystal structure determination revealed a considerable deviation from planarity.[8] Thus, the existence of [4]metacyclophane (**1a**) seemed overdue. Our first attempt to form **1a** by irradiation of its Dewar analogue (**2a**)[9] failed but gave instead quantitatively the corresponding prismane valence isomer.[10] Recently, we were able to provide evidence for the formation of **1a** as an intermediate by heating **2a** in an ampoule or under GC conditions; it dimerized in a characteristic and unique reaction via two consecutive cycloaddition reactions to give cage dimers.[11] We now present further evidence for the formation of [4]metacyclophane at higher temperature in the gas phase. This evidence finds support in similar behavior of [5]metacyclophane (**1c**).

Table I. Calculated Heats of Formation[a] of 1–4 and 6

compd	$\Delta H_f°$	compd	$\Delta H_f°$
1a	76.5[b]	**4a**	77.1
1c	45.7[b]	**4c**	78.0
2a	74.6	**6a**	73.1[c]
3a	136.2[d]	**6c**	68.2[c]

[a] MNDO;[19] in kcal mol^{-1}. [b] Reference 12. [c] Calculated by standard group increments according to Benson.[20] [d] The value was calculated by using the MNDO value for 2,6-dimethyl Dewar benzene,[12] which was adapted by group increments.[20]

Scheme I



Results and Discussion

When **2a** was subjected to flash vacuum thermolysis (FVT) at 400 °C, tetralin (**5a**) and methyl-substituted indans (**8a**, **10a**) were formed in a ratio of about 90:5:5 (recovery, 50%). The key step in this thermolysis is proposed to be the formation of **1a** from **2a**; this reaction is only slightly endothermic according to MNDO calculations (Table I, Scheme I). In sharp contrast, the direct homolytic bond cleavage from **2a** to **3a** is highly endothermic ($\Delta\Delta H_f°$ = 61.2 kcal mol^{-1}) and may be disregarded. Under the FVT conditions, **1a** is not expected to be stable as it will try to relieve its strain. Due to its low concen-

(1) For a recent review, see: *Cyclophanes*; Keehn, P. M., Rosenfeld, S. M., Eds.; Academic: New York, 1983.
(2) Jenneskens, L. W.; De Kanter, F. J. J.; Kraakman, P. A.; Turkenburg, L. A. M.; Koolhaas, W. E.; De Wolf, H. H.; Bickelhaupt, F.; Tobe, Y.; Kakiuchi, K.; Odaira, Y. *J. Am. Chem. Soc.* **1985**, *107*, 3716.
(3) (a) Tobe, Y.; Kaneda, T.; Kakiuchi, K.; Odaira, Y. *Chem. Lett.* **1985**, 1301. (b) Kostermans, G. B. M.; De Wolf, W. H.; Bickelhaupt, F. *Tetrahedron Lett.* **1986**, *27*, 1095. (c) Kostermans, G. B. M.; De Wolf, W. H.; Bickelhaupt, F. *Tetrahedron* **1987**, *43*, 2955.
(4) (a) Landheer, I. J.; De Wolf, W. H.; Bickelhaupt, F. *Tetrahedron Lett.* **1974**, 2813. (b) Kostermans, G. B. M.; Bobeldijk, M.; De Wolf, W. H.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1987**, *109*, 2471.
(5) (a) Tsuji, T.; Nishida, S. *J. Chem. Soc., Chem. Commun.* **1987**, 1189. (b) Tsuji, T.; Nishida, S. *J. Am. Chem. Soc.* **1988**, *110*, 2157.
(6) (a) Van Straten, J. W.; De Wolf, W. H., Bickelhaupt, F. *Tetrahedron Lett.* **1977**, 4667. (b) Turkenburg, L. A. M.; Blok, P. M. L.; De Wolf, W. H.; Bickelhaupt, F. *Tetrahedron Lett.* **1981**, *22*, 3317.
(7) (a) Turkenburg, L. A. M.; De Wolf, W. H.; Bickelhaupt, F. *Tetrahedron Lett.* **1983**, *24*, 1817. (b) Jenneskens, L. W.; De Kanter, F. J. J.; Turkenburg, L. A. M.; De Boer, H. J. R.; De Wolf, W. H.; Bickelhaupt, F. *Tetrahedron* **1984**, *40*, 4401.
(8) Jenneskens, L. W.; Klamer, J. C.; De Boer, H. J. R.; De Wolf, W. H.; Bickelhaupt, F.; Stam, C. W. *Angew. Chem.* **1984**, *96*, 236.
(9) Turkenburg, L. A. M.; Van Straten, J. W.; De Wolf, W. H.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1980**, *102*, 3256.
(10) Kostermans, G. B. M.; Hogenbirk, M.; Turkenburg, L. A. M.; De Wolf, W. H.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1987**, *109*, 2855.
(11) Kostermans, G. B. M.; Van Dansik, P.; De Wolf, W. H.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1987**, *109*, 7887.

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Scheme II

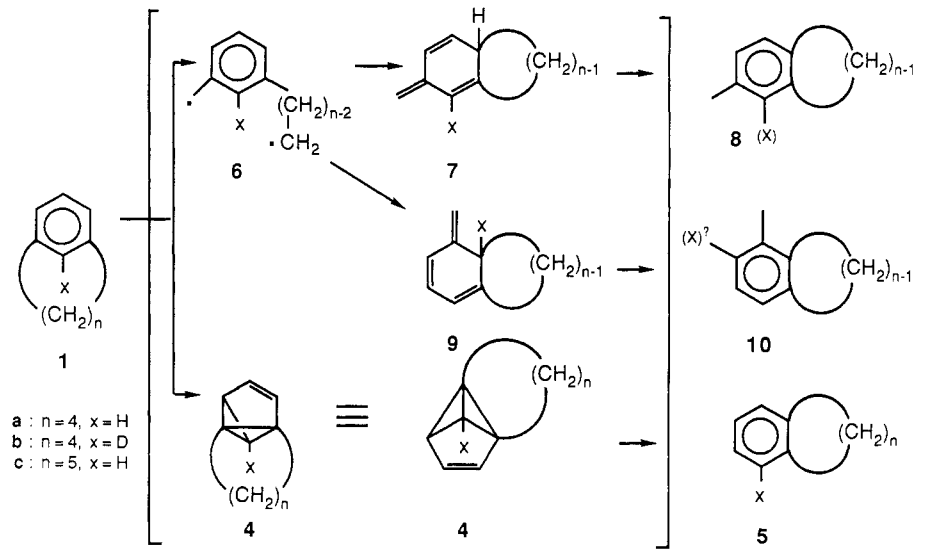


Table II. Product Distribution of the FVT Experiments

entry	educt	T, °C	recovery,[a] %	products[b]				
				educt	5	8	10	dimers[c]
1	**2a**	400	50		87	5	5	3
2	**2a**	500	25		89	5	5	<1
3	**1c**	500	80	82	2	9	7	
4	**1c**	600	60		2	60	38	

[a] Determined from ^{1}H NMR analysis with C_6H_6 as internal standard. [b] In percentages of the pyrolysate determined from ^{1}H NMR and GCMS analysis. [c] See ref 11.

tration in the gas phase, **1a** cannot dimerize as it did in our previous experiments.[11] A feasible process is cleavage of one of the benzylic bonds to form the diradical **6a** (Scheme II), which is of comparable energy ($\Delta H_f°$(**1a**) = 76.5 kcal mol^{-1},[12] $\Delta H_f°$(**6a**) = 73.1 kcal mol^{-1}). This diradical can form a five-membered ring to give **7a** or **9a**, which react further to the two possible methyl-substituted indans **8a** and **10a**, respectively. Although the spin density in the benzylic radical is usually higher at the para position as compared to the ortho position,[13] this difference is not reflected in the product distribution, which shows equal amounts of **8a** and **10a**.

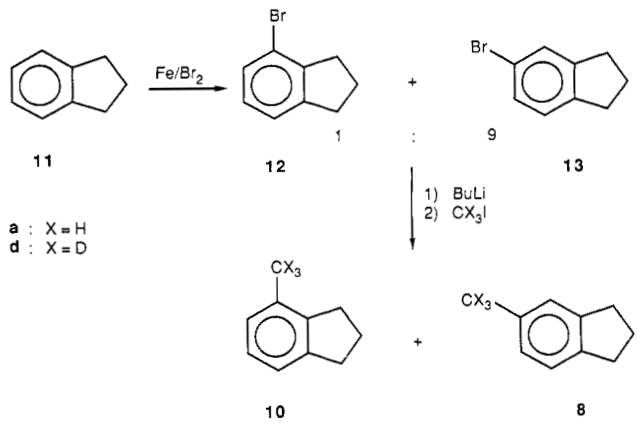
The second route available for **1a** to relieve its strain is the symmetry-allowed[14] transformation to its benzvalene isomer **4a**, which, under the reaction conditions, rearranges to the aromatic ortho isomer tetralin (**5a**). Although **4a** is calculated to have a $\Delta H_f°$ = 77.1 kcal mol^{-1}, which is 4.0 kcal mol^{-1} higher than that of **6a**, the experimental result shows that **1a** rearranges preferentially to the benzvalene isomer. Two factors may be responsible. In the first place, $\Delta H_f°$ (**4a**) (MNDO[19]) and $\Delta H_f°$ (**6a**) (increments[20]) were calculated by different approaches and may not be fully comparable. Secondly, even it they were, the activation energies need not necessarily parallel the ground-state energies. For instance, the ground-state energy of **6a** includes the full resonance stabilization of its benzyl radical subunit; this resonance will not be fully developed in the transition state, especially because the extreme conformational rigidity of **1a**[12] enforces an oblique, nonideal orientation of the developing benzylic p orbital and the π-system of the aromatic nucleus. In fact, the insensitivity of the product ratios to a change of temperature (Table II) indicates that for **1a** → **4a** and **1a** → **6a**, $\Delta\Delta H^‡$ is close to zero. This in turn means that the preferential formation of **5a** (via **4a**) is governed by the more positive activation entropy of this process. The reasons for this are not fully understood.

The proposed mechanism was supported by deuterium labeling experiments. Introduction[21] of deuterium at the position between the bridge gave **2b**, which on FVT yielded the expected **5b**, **8b**, and **10b** (Scheme II). In **5b**, the label was shown to be fully retained by GCMS analysis and to be located at C-5 by ^{13}C NMR spectroscopy: C-6 and C-7 had a slightly different chemical shift caused by an isotope shift[22] for C-6 (δ(C-6) 125.35, δ(C-7) 125.24 ppm), and the intensity of the signal for C-5 and C-8 (δ 129.1 ppm) was only 50% of its value in **5a**.[23] In **8b** the label was also fully retained, but in **10b**, 50–60% of the deuterium was lost.

These results are not easy to reconcile with a plausible alternative to the proposed thermal reaction mode, i.e. an acid-catalyzed wall reaction. Nevertheless and even though the latter mode of reaction is less likely under the conditions of FVT,[24] we decided to investigate the behavior of **1b** (thermally formed from **2b**[11]) in the presence of acid. For this purpose, **2b** was heated in an ampoule together

(12) Jenneskens, L. W.; De Kanter, F. J. J.; De Wolf, W. H.; Bickelhaupt, F. *J. Comput. Chem.* **1987**, *8*, 1154. The reported value for **1a** ($\Delta H_f°$ = 77.1 kcal mol^{-1}) was found to improve slightly to $\Delta H_f°$ = 76.5 kcal mol^{-1} due to a more precise termination criterium.
(13) Dixon, W. T.; Norman, R. O. C. *J. Chem. Soc.* **1964**, 4857.
(14) Mulder, J. J. C. *J. Am. Chem. Soc.* **1977**, *99*, 5177.
(15) Turkenburg, L. A. M. Thesis, 1982, Vrije Universiteit, Amsterdam.
(16) Rae, I. D.; Umbrasas, B. N. *Aust. J. Chem.* **1975**, *28*, 2669.
(17) Sasson, I.; Labovitz, J. *J. Org. Chem.* **1975**, *40*, 3670.
(18) Adamczyk, M.; Watt, D. S.; Netzel, D. A. *J. Org. Chem.* **1984**, *49*, 4226.
(19) Dewar, M. J. S.; Thiel, W. J. *J. Am. Chem. Soc.* **1977**, *99*, 4899.
(20) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1968.
(21) The details of the preparation of **2b** will be published in a forthcoming paper; the synthesis followed essentially that described for **2a**.[9]
(22) Berger, S.; Diehl, B. W. K. *Tetrahedron Lett.* **1987**, *28*, 1243.
(23) Because of the small amount of material (10 mg of **2b**), we were not able to detect the low intensity triplet of C-5 itself.
(24) Brown, R. F. C. *Pyrolytic Methods in Organic Chemistry*; Academic: New York, 1980.

Scheme III



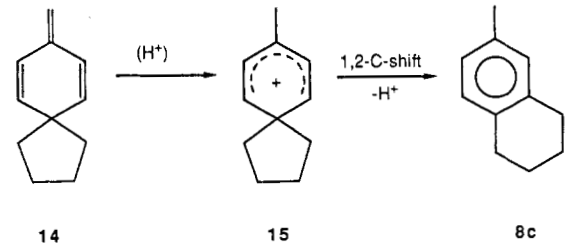
with a 5-fold molar amount of trifluoroacetic acic at 150 °C. Apparently, **2b** is largely polymerized under these conditions, but GCMS analysis clearly indicated that only **5b** (12%) was formed, together with an unidentified product of the composition of [**2b** + CF_3COOH]; **8b** and **10b** were completely absent (GCMS and ^1H NMR analysis). Another important observation is that **5b** obtained in this experiment had lost 32% of its deuterium label, in contrast to the 100% retention in the thermal experiment. These findings make acid catalysis in the formation of **5b** on FVT highly unlikely, and similarly, the 100% retention of the label in **8b** on FVT is not in line with an acid-catalyzed transformation.

The interesting question of how the hydrogen (or deuterium) migration in the aromatization of the intermediates **6** and **9** to **8** and **10**, respectively, takes place needs further investigation, but some relevant features can be pointed out at this stage. In the first place, the label is not incorporated into the methyl groups of **8** and **10** within the limits of accuracy, which is estimated to be 5–10%.[25] This follows from the mass spectroscopic analysis of **8d** and **10d** (synthesized as shown in Scheme III), which revealed that the methyl groups of the methylindanes are cleaved from the molecular ion essentially as such and without prior scrambling with other hydrogens (see the Experimental Section). In this respect, **8** and **10** differ from other methyl-substituted aromatics such as toluene,[26] and this remarkable feature deserves further investigation. In the present context, the identical deuterium content of the $M^{\bullet+}$ and the $[M - Me]^+$ ions from **8b** and **10b** allows the conclusion that deuterium is retained at the aromatic ring.

A second interesting and slightly disturbing aspect is the loss of about 50–60% label in **10b**. A referee pointed out that contrary to **6**, intermediate **9** has the possibility of a rapid 1,5-hydrogen shift, which will lead to H/D scrambling. However, it is not clear at the moment how this might lead to loss of label in **10** (which does not occur in **8**). We are activily pursuing this intriguing question.

The results presented so far strongly suggest that the highly strained [4]metacyclophane is an intermediate in the thermolysis reaction of its Dewar isomer. In order to further support this interpretation, it would have been desirable to subject the Dewar isomer of [5]metacyclophane to an analogous FVT reaction; however, this Dewar isomer is not known.[6,15] Therefore, we used [5]-metacyclophane (**1c**) itself to investigate its FVT behavior.

Scheme IV



While this makes the analogy less close, it offers, on the other hand, the advantage to study the behavior of a strained metacyclophane directly, which is not possible in the tetramethylene series.

When we subjected **1c** to FVT, the only products were methyl-substituted tetralins (**8c**, **10c**). A small amount of cycloheptabenzene **5c** (2%) was detected, but this ortho isomer was probably already present in the educt **1c** since the two could not be separated by preparative gas chromatography. Moreover, the amount of **5c** in both FVT experiments (Table II, entries 3 and 4) was equal, which is unlikely if its formation were correlated to the disappearance of **1c**. The ratio of **8c**:**10c** was about 3:2 in both cases. This may be caused by the higher spin density of the benzylic radical[13] at the para position or by a steric effect which might be expected to oppose attack at the ortho position. As mentioned above, this very slight preference for the formation of **8** was not observed in the lower homologue. A rationalization of the product distribution of **5** versus **8** + **10** for the [4]- and [5]metacyclophane series can be given on the basis of thermodynamic arguments. If we compare the heats of formation of **4c** and **6c**, the latter is more stable by about 10 kcal mol^{-1} (Table I). Even keeping in mind that as discussed for the lower homologue the diradical **6c** may have been calculated too stable, the energy gap is undoubtedly much larger in the **c** (pentamethylene) series. This thermodynamic ground state advantage is apparently reflected in the transition state to make the formation of **6c** compete effectively with that of **4c**. Comparison of the calculated geometries of **1a** and **1c** reveals[12] that the two bridgehead carbons in **1a** are much closer; as bond formation between them is a logical first step in benzvalene formation, this may be another factor in making the benzvalene route more important in the **b** (tetramethylene) series.

The large difference in temperature needed to achieve complete conversion of **2a** (<400 °C) and **1c** (>500 °C) (Table II) can be rationalized as follows. The $\Delta\Delta H_f°$ between **2a** and **1a** is only 1.9 kcal mol^{-1}. Still, this aromatization needs much more thermal energy than other Dewar benzene aromatizations, which generally occur in the range between 0 and 100 °C;[27] even if one keeps in mind that the effective reaction temperatures are lower than the oven temperatures of FVT by 100–200 °C,[24] the onset for the aromatization of **2a** is around 200–300 °C. The formation of **1a** is the rate-determining step, and once it is formed, the two possible routes from **1a** to **4a** or **6a** are nearly thermoneutral ($\Delta\Delta H_f°$ = 0.6 kcal mol^{-1} for **4a**; $\Delta\Delta H_f°$ = −3.4 kcal mol^{-1} for **6a**) so that both reactions will take place easily. The situation is very different in the case of **1c**; both routes to the less strained derivatives **4c** and **6c** are highly endothermic in the first step. The diradical pathway to **6c** involves a reaction enthalpy of 22.5 kcal mol^{-1}, and the benzvalene route to **4c** is endothermic by

(25) The program Mass Cluster was used; it was developed at the Free University by Drs. N. J. R. van Eikema Hommes, whom we thank for providing the program to us.

(26) Beynon, J. H.; Saunders, R. A.; Williams, A. E. *The Mass Spectra of Organic Molecules*; Elsevier: Amsterdam, 1968; p 122.

(27) Van Straten, J. W.; Turkenburg, L. A. M.; De Wolf, W. H.; Bickelhaupt, F. *Recl. Trav. Chim. Pays-Bas* **1985**, *104*, 89, and references cited.

32.3 kcal mol^{-1}; the activation energies must be higher still. This explains the higher reaction temperatures needed for **1c** as compared to **2a**.

The structures of **8a** and **10a** were derived from their spectral data[18] and from an independent synthesis of both compounds as outlined in Scheme III. The spectral data of **8c**[16] and **10c**[17] were in agreement with literature data; in addition, an independent synthesis of **8c** was performed as outlined in Scheme IV.[15]

Experimental Section

^{1}H NMR spectra were recorded on a Bruker WM 250 spectrometer. ^{13}C NMR spectra were recorded on a Bruker WM 250 at a frequency of 62.89 MHz. Signals assignments marked by one or two asterisks (* or **) may have to reversed. GCMS spectra were recorded on a HP 5890 MSD spectrometer operating at 70 eV. HRMS spectra were measured on a Varian CH-5-DF spectrometer at 70 eV. The FVT equipment has been described before.[28] In the present experiments, we used a 28-cm Al_2O_3 tube and a pressure of 0.02 mbar.

Flash Vacuum Thermolysis of 2a. A solution of **2a** (4 mg, 3×10^{-5} mol) in pentane (50 μL) was cooled to −78 °C. Then, vacuum was applied in order to evaporate **2a** into the hot zone. Within 10 min, the material had evaporated into the hot zone (400 °C or 500 °C, see Table II). The pyrolysate was trapped on a cold finger at −78 °C. The products were washed off with $CDCl_3$. ^{1}H NMR and GCMS analysis indicated a product composition of 87% **5a**, 5% **8a**, and 5% **10a** (^{1}H NMR, GC retention times, and mass spectra were identical with those of independently synthesized samples, vide infra) as well as 3% of dimeric products[11] (total recovery 25–50%).

Flash Vacuum Thermolysis of 2b. The experiment was carried out with **2b** (10 mg, 0.076 mmol) in pentane (100 μL) as described for **2a**. **5b**: $^{13}C\{^1H\}$ NMR (62.89 MHz, $CDCl_3$, 300 K) δ 137.0 (C(4a,8a)), 129.1 (C(8)), 125.35 (C(6)) (isotope shift of $\Delta\delta$ + 0.11 ppm[22]), 125.24(C(7)), 29.38(C(1)*), 29.33(C(4)*), 23.2 (C-(2,3)); mass spectral analysis of the molecular ion clusters of **5b**, **8b**, and **10b** gave **5b**$^{\bullet+}$ (D_1 = 100%), **8b**$^{\bullet+}$ (D_1 = 100%), **10b**$^{\bullet+}$ (D_0 = 53%, D_1 = 45%, D_2 = 2%). Analysis of the $[M - Me]^+$ cluster yielded $[\mathbf{8b} - Me]^+$ (D_0 = 10%, D_1 = 90%), $[\mathbf{10b} - Me]^+$ (D_0 = 60%, D_1 = 40%).

Flash Vacuum Thermolysis of 1c. The experiment was carried out as described above with **1c** (1 mg, 0.7×10^{-2} mmol) in pentane (100 μL). The product distribution at 500 °C and 600 °C was determined by ^{1}H NMR and GCMS analysis (Table II, entry 3). ^{1}H NMR,[16,17] GC retention times (**8c** only), and mass spectra were in agreement with literature data and with those of an independently synthesized sample (**8c** only, see Scheme IV). In larger runs (about 10 mg of **1c**), **8c** and **10c** were separated by preparative gas chromatography (10% Carbowax 20M, 1.5 m, 150 °C).

6-Methyltetralin (8c): ^{1}H NMR (250 MHz, $CDCl_3$, 298 K) δ 6.98 (d, J = 8 Hz, 1 H, H(7)*), 6.95 (d, J = 8 Hz, 1 H, H(8)*), 6.90 (s, 1 H, H(5)), 2.73 (m, 4 H, H(1,4), 2.29 (s, 3 H, CH_3), 1.78 (m, 4 H, H(2,3)); MS, m/z (relative intensity) 146 (78) ($M^{\bullet+}$), 131(100). *Independent preparation*: When a NMR solution of **14**[29] was kept overnight in $CDCl_3$, **8c** was the only product formed.[15] $CDCl_3$ probably contained traces of DCl, which were responsible for this process.

5-Methyltetralin (10c): ^{1}H NMR (250 MHz, $CDCl_3$ 298 K) δ 7.1–6.9 (m, 3 H), 2.78 (t, J = 6 Hz, 2 H, H(4)), 2.63 (t, J = 6 Hz, 2 H, H(1)), 2.22 (s, 3 H, CH_3), 1.78 (m, 4 H, H(2,3)); MS, m/z (relative intensity) 146 (71) ($M^{\bullet+}$), 131 (100).

Synthesis of 4- and 5-Bromoindan (12, 13). To a solution of indan (**11**) (2.0 g, 16.9 mmol) in *n*-hexane (40 mL) was added Fe powder (0.1 g, 1.8 mmol) and Br_2 (2.7 g, 17 mmol). The mixture was allowed to react for 2.5 h at room temperature in the absence of light after which a saturated $NaHCO_3$ solution (50 mL) was added. The mixture was extracted with pentane and dried with $MgSO_4$. Concentration under reduced pressure gave 3.3 g of a yellow oil, which after distillation (117 °C, 15 mmHg) yielded 1.84 g (9.3 mmol, 55%) of a mixture of **12** and **13** as a colorless oil (ratio of 1:9). Separation was achieved by preparative gas chromatography (1.5 M, 15% SE-30, 60 mL/min H_2 as carrier gas, 120 °C).

4-Bromoindan (12): ^{1}H NMR (250 MHz, $CDCl_3$, 298 K) δ 7.29 (d, J = 8 Hz, 1 H, H(5)), 7.15 (d, J = 8 Hz, 1 H, H(7)), 7.00 (t, J = 8 Hz, 1 H, H(6)), 3.02 (t, J = 7.5 Hz, 2 H, H(3)), 2.96 (t, J = 7.5 Hz, 2 H, H(1)), 2.09 (quin, J = 7.5 Hz, 2 H, H(2)); MS, m/z (relative intensity) 198 (41), 196 (43) ($M^{\bullet+}$) 117 (100).

5-Bromoindan (13): ^{1}H NMR (250 MHz, $CDCl_3$, 298 K) δ 7.36 (s, 1 H, H(4)), 7.25 (d, J = 8.0 Hz, 1 H, H(6)), 7.09 (d, J = 8.0 Hz, 1 H, H(7)), 2.90 (t, J = 7.5 Hz, 2 H, H(3)), 2.86 (t, J = 7.5 Hz, 2 H, H(1)), 2.08 (quin, J = 7.5 Hz, 2 H, Hn2)); MS, m/z (relative intensity) 198 (39) ($M^{\bullet+}$), 196 (42), 117 (100); HRMS calcd for $C_9H_9{}^{79}Br$ 195.9888, found 195.9879.

Synthesis of 4- and 5-Methylindan (10a, 8a). To a solution of a mixture of **12** and **13** (0.25 g, 1.27 mmol) in Et_2O (10 mL) was added a solution of BuLi (1.6 M, 4 mL, 6.4 mmol) at −50 °C. The solution was allowed to warm up to room temperature, stirred for another 30 min, and then cooled to −50 °C, and MeI was added (0.5 mL, 8 mmol), after which the temperature was raised to room temperature. The solution was quenched with water, extracted with diethyl ether, and dried over $MgSO_4$. Concentration under reduced pressure yielded 0.16 g of a slightly yellow oil that consisted of 40% indan (64 mg, 0.54 mmol, 42%), 54% **8a** (86 mg, 0.65 mmol, 52%) and 6% (10 mg, 0.07 mmol, 6%) **10a**; the ratio **8a**:**10a** (8.7:1) reflects that of **13**:**12** (9:1) (vide supra). The products were separated by preparative gas chromatography (15% Carbowax 20M, 1.5 M, 60 mL/min H_2 as carrier gas, 100 °C). ^{1}H NMR and MS spectral data for **8a** and **10a** were identical with literature data.[18]

Synthesis of [1′,1′,1′-$^2H_3$]-4- and 5-Methylindan (10d, 8d). The experiment was carried out as described above for **8a** and **10a** with the same mixture of **12** and **13** (25 mg, 0.13 mmol), BuLi (1.6M, 1 mL, 1.6 mmol), and CD_3I (230 mg, 1.6 mmol). The product mixture consisted of **8d** and **10d** in a ratio of 9:1 (GC, ^{2}H NMR). Yield after preparative GLC (15%, SE-30, 1.5 M, 60 mL/min H_2 as carrier gas, 100 °C): 4 mg (24%) of **8d** and **10d**.

[1′,1′,1′-$^2H_3$]-5-Methylindan (8d): ^{1}H NMR spectrum was identical with that of **8a** except for the absence of the Me group signal; ^{2}H NMR (38.39 MHz, 300 K, $CHCl_3$) δ 2.30 (s); MS, m/z (relative intensity) 135 (73) $M^{\bullet+}$, 117 (100). The $M^{\bullet+}$ cluster of **8d** was fitted[25] on **8a** and yielded D_3 = 97%, D_4 = 3%. The $[M - Me]^+$ analysis gave D_0 = 85%, D_1 = 11%, D_2 = 2%, and D_3 = 2%, which means that 15% of the label scrambles in the expulsion of the methyl group.

[1′,1′,1′-$^2H_3$]-4-Methylindan (10d): ^{1}H NMR spectrum was identical with that of **10a** except for the absence of the Me group signal; ^{2}H NMR (38.39 MHz, 300 K, $CHCl_3$) δ 2.25 (s); MS, m/z (relative intensity) 135 (52) $M^{\bullet+}$, 117 (100). The results of the analysis[25] of the $M^{\bullet+}$ and $[M - Me]^+$ clusters gave ($M^{\bullet+}$) D_3 = 97%, D_4 = 2%, D_5 = 1% and ($[M - Me]^+$) D_0 = 91%, D_1 = 4%, D_2 = 3%, D_3 = 2%.

Thermolysis of 2b in the Presence of Acid. An ampoule containing **2b** (5 mg, 0.04 mmol) and CF_3CO_2H (14 μL, 0.2 mmol) was heated for 5 min at 150 °C.[11] The product mixture contained neither **8b** nor **10b** (GCMS analysis) while **5b** had lost 32% of its deuterium label. Also a product with mass m/z 247 was formed, which is possibly the CF_3COOH adduct of **2b**. Purification of **5b** by preparative GC gave 0.6 mg (12%). The low yield of this reaction is probably caused by a rapid polymerization of **2b** in concentrated CF_3CO_2H.

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(28) Jenneskens, L. W.; De Wolf, W. H.; Bickelhaupt, F. *Tetrahedron* **1984**, *40*, 3117.

(29) Van Straten, J. W.; Landheer, I. J.; De Wolf, W. H.; Bickelhaupt, F. *Tetrahedron Lett.* **1975**, 4499.