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The Thermal Aromatization of Methyl-1,3-cyclohexadienes – An Important Argument against Commonly Accepted Sigmatropic 1,7-H-Shift Reactions

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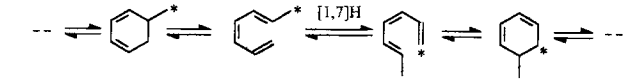
Dedicated to Professor Dr. Wilhelm Pritzkow on the Occasion of his 65th Birthday

Abstract. It has been demonstrated that the methyl and ring C-atoms of methyl-1,3-cyclohexadienes interchange their positions intramolecularly during the thermal conversion to toluene at temperatures above 600 °C in a quartz flow system. Gas phase pyrolysis of double ^{13}C-labeled methyl-1,3-cyclohexadienes with ^{13}C-labels for the primary and the tertiary C-atom gave definite ^{13}C-distribution patterns in the aromatic ring systems of the formed toluene as well as benzene with far-reaching similarities. The NMR data of the [$^{13}C_2$]toluene isotopomers definitely rule out that the observed integration of the methyl C-atom into the ring system proceeds via the hitherto well-established sequence: electrocyclic ring opening of the 5-methyl-1,3-cyclohexadiene to 1,3,5-heptatriene, its sigmatropic 1,7-H shift and ensuing recyclization of the 1,3,5-heptatriene to methyl-1,3-cyclohexadienes.

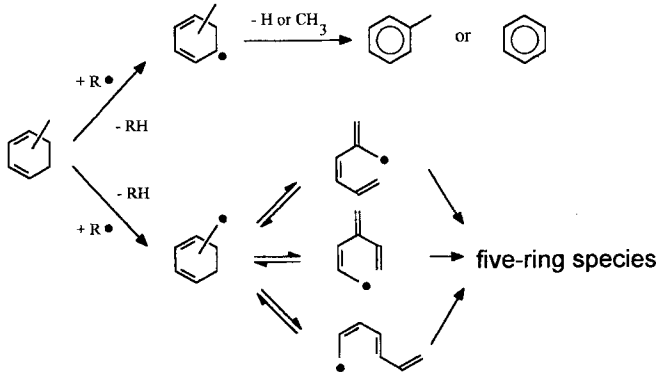
Introduction

Cyclohexadienes are the mostly considered intermediates immediately preceding the aromatics in catalytic dehydrogenation or in free radical processes involving successive loss of alkyl groups and/or hydrogen atoms [1]. On pyrolyzing [methyl-^{14}C]methyl-1,3-cyclohexadienes, we recently observed the formation of [ring-^{14}C]-labeled toluene and benzene besides the expected [methyl-^{14}C]toluene and unlabeled benzene [2]. Since under these reaction conditions a subsequent C-scrambling of the already formed toluene (e. g., via benzyl ⇌ tropylium radical isomerization) occurs only to less than 2 %, two alternative pathways were taken into account for the mechanistic interpretation of these surprising results:

(i) a sequence involving preliminary electrocyclic ring opening followed by sigmatropic [1,7]H shift and recyclization (Scheme 1)



(ii) a radical-chain process starting by H-abstraction and followed by unimolecular hydrogen and/or methyl loss including the formation of five-ring species as immediate precursors of the aromatics (Scheme 2).



By reason of the importance of C-scrambling reactions in thermal aromatization processes in general and automerization of nonaromatic C-ensembles in particular, the observation described above certainly deserves more careful mechanistic studies than have been carried out to date.

On the assumption that the sequence ring opening → [1,7]H shift → ring closure (Scheme 1) does not present an important pathway in the presence of radical-chain processes as shown by a recently published paper [1] according to which cyclohexadienes are again considered the actual aromatic precursors in thermal hydrocarbon conversion, we started further investigations on gas phase pyrolysis of methyl-1,3-cyclohexadienes and [$^{13}C_2$]methyl-1,3-cyclohexadienes with one ^{13}C-label in the methyl group and the other one at the ring position attached to the ^{13}C-methyl group (see Table 1).

Table 1 Composition of the [methyl, ring-$^{13}C_2$]methyl-1,3-cyclohexadienes/[methylene, ring-$^{13}C_2$]-3-methylene-cyclohexene fraction[a] used as feedstock for pyrolysis experiments (• = ^{13}C)

compound	 1	 2	 3	 4
percentage in the fraction	63	17	2	18

a) the corresponding unlabeled fraction holds the compounds in the same percentage

Table 2 Composition of the reaction products of the gas phase pyrolysis of the methyl-1,3-cyclohexadienes fraction given in Table 1 (τ = 0.3 s; $n_{N2} : n_{HC}$ = 50 : 1; data given in selectivity units S[a])

reaction temperature (°C)	600	700
degree of conversion (%)	5	98
gaseous products $\leq C_4$ [b]	ca. 35	ca. 54
cyclopentadiene	0.1	0.5
fulvene	–	ca. 0.1
2-methylfulvene	–	< 0.1
3-methylfulvene	–	ca. 0.1
6-methylfulvene	–	ca. 0.1
C_6H_x (x = 6,8)	3.2	5.2
benzene	17.0	29.8
toluene	59.3	23.6
dimethylfulvenes	–	< 0.1
ethylbenzene	traces	1.4
xylenes	traces	2.1
styrene	traces	1.4
products $>C_8$	1.0	9.0

a) S = moles formed per 100 moles converted, b) H_2, CH_4, C_2H_4, C_2H_6, 1,3-C_4H_6

Results

Pyrolysis of Methyl-1,3-cyclohexadienes

A mixture of the methyl-1,3-cyclohexadiene isomers and 3-methylenecyclohexene (Table 1) was synthesized (see Experimental), thermally converted and the reaction products were carefully analysed to detect and identify all the liquid products which were formed in portions of more than 0.1 wt-%. The conversion was carried out in a lab-scale tubular reactor (V_R = 10 ml, d_i = 10 mm, quartz) at 600 to 700 °C, at a residence time of about 0.3 s and in the presence of oxygen-free nitrogen ($n_{N2} : n_{HC}$ = 50 : 1). The gaseous products (as a sum) and the liquid products formed at 600 and 700 °C are listed in Table 2. The composition of the starting hydrocarbon mixture, the cracked liquids, and the overall product samples were analyzed by capillary GC.

The peak areas were integrated electronically, and the structure assignments of unknown GC peaks were made by comparison of their GC retention time behaviour with those of authentic compounds available from other investigations [2–4] as well as by their mass and infrared spectra (GC-MS, GC-FTIR).

The results listed in Table 2 show clearly that the liquid pyrolyzate contains only intermediates with five-ring structures together with unconverted starting compounds and the expected aromatics (benzene, toluene, and higher boiling substances ones formed by synthetic reactions).

Only traces of acyclic intermediates and bicyclo[3.1.0] hexene-type hydrocarbons [1] could be detected in the liquid pyrolyzate.

The formation of toluene and benzene depends significantly on the reaction temperature (Fig. 1). The formation of benzene via demethylation of toluene can, however, not be of significance, because under these reaction conditions toluene is demethylated to an extent of only some 2 %. Therefore, we conclude that the C_7-ensemble of the methyl-1,3-cyclohexadienes obviously loses the methyl group before or during the aromatization step.

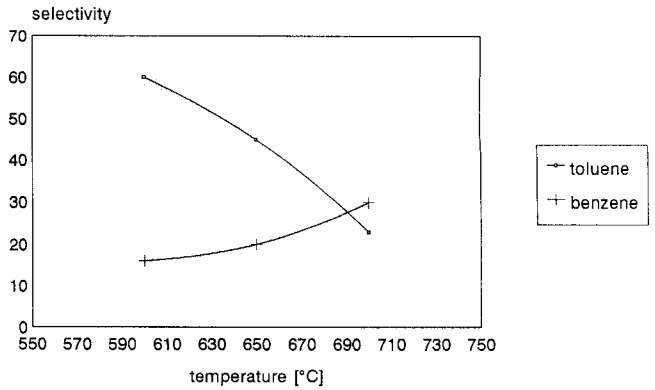


Fig. 1 Dependence of the benzene and toluene selectivity on the reaction temperature

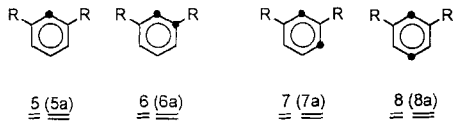
Pyrolysis of [Methyl, ring-$^{13}C_2$]methyl-1,3-cyclohexadienes

The so far unknown doubly ^{13}C-labeled methyl-1,3-cyclohexadienes with methyl, ring ^{13}C-^{13}C-bond were synthesized as described in the Experimental section and analyzed by means of capillary GC, GC-MS and NMR. The composition of the obtained C_7H_{10}-fraction is listed in Table 1. It consists of the three methyl-1,3-cyclohexadienes isomers **1** to **3** and 3-methylenecyclohexene **4**, which on its part isomerizes rapidly to the methyl-1,3-cyclohexadienes at temperatures above 500 °C [2].

When this fraction was subjected in the same pyrolysis unit as described above at 700 °C (0.3 s) the distribution of the products corresponded with that given in Table 2 for the unlabeled substances. Then, benzene and toluene of the liquid pyrolyzate were separated by preparative GC with yields of about 90 %.

Spectroscopic Analysis of the Toluene and Benzene Fraction

Since in gas phase pyrolysis [methyl-^{14}C]methyl-1,3-cyclohexadienes give ^{14}C-labeled benzene and [ring-^{14}C]-labeled toluene besides unlabeled benzene and [methyl-^{14}C]-labeled toluene [2] one has in principle to reckon with the formation of one [$^{13}C_1$]-benzene (**5**) and three [$^{13}C_2$]benzene isotopomers (ortho- (**6**), meta- (**7**) and para- (**8**), Scheme 3) as well as of four [methyl, ring-$^{13}C_2$]- (**9–12**) and nine [ring-$^{13}C_2$]toluene isotopomers (**13–21**) (Table 5).



5 (5a) 6 (6a) 7 (7a) 8 (8a)

• = ^{13}C 5 - 8 : R = H 5a - 8a : R = NO_2

Before proceeding with the ^{13}C-NMR analysis, both the fractions were first analysed by capillary GC. It follows from that that in the benzene fraction benzene (93 %) was accompanied by about 7 % of methylcyclopentadienes and traces of pentafulvene, while the toluene (87 %) was contaminated by 11 % of unconverted methyl-1,3-cyclohexadienes and small amounts of 2-, 3- and 6-methylfulvenes, vinylcyclopentadienes, methyldihydrofulvenes and isopropenylcyclopentadienes. By mass spectrometric analysis, the percentages of di- and mono-labeled benzene in the corresponding fraction were acutally found to be 57.4 % and 42.6 %, respectively. Non- and trilabeled benzenes could not be detected, they are at best formed in traces. The toluene on its part consisted of more than 99 % of doubly ^{13}C-labeled isotopomers.

^{13}C-NMR Analysis of the Benzene Fraction

The ^{13}C-NMR spectroscopic analysis of the benzene fraction was carried out after its nitration to a mixture of dinitrobenzenes following the procedure published by Scott et al. [5]. The signals of the ^{13}C-atom between the two nitro groups in the m-dinitrobenzenes centred at 119ppm in the high-field region are decisive for the determination of the ratio of [o-$^{13}C_2$]-, [m-$^{13}C_2$]- and [p-$^{13}C_2$]benzene. Such signals can only be stemming from four of the thirteen possible compounds. They are depicted in Scheme 3 (compounds **5a-8a**).

The other nine isomers hold a ^{12}C-atom in the 2-position; they do not disturb the determination of the contents of **5** to **8** in the nitrated benzene fraction. The signals for **5** to **8** from the ^1H-noise decoupled ^{13}C-NMR spectrum of the nitrated benzene fraction are listed in Table 3. It shows only the signals of ^{13}C-enriched C-positions because signals of ^{13}C-atoms in positions occupied in natural abundance could not be distinguished from the back ground noise. Taking published coupling constants [6] of $^1J_{cc}$ = 70 Hz (60 ... 80 Hz) for ortho-$^{13}C_2$ in a benzene ring, of $^2J_{cc}$ = 0–2 Hz for metha-$^{13}C_2$ and $^3J_{cc}$ = 7 Hz (5–8 Hz) for para-$^{13}C_2$ into account and based on the relative intensities of the signals from integration of the peaks centered at 119 ppm and listed in Table 3, the signal C can be assigned to compound **8** (1 %), signal B to **6** (24 %) and signal A to **5** and **7** (sum 76 %). From that, the following relations can be established:

- **5** : (**6** + **7** + **8**) = 42.6 : 57.4 (MS)
- **6** : **8** = 10.5 : 0.1 (NMR)
- (0,5 × **5** + **7**) : (**6** + **8**) = 46.5 : 53.5 (NMR)

which allows one to calculate the composition of the ^{13}C-labeled benzenes in percentages resulting in **5** : **6** : **7** : **8** = 43 : 24 : 33 : 1.

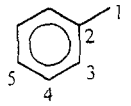
Table 3 NMR signals of ^{13}C-atoms positioned between those C-atoms, which are substituted by nitro groups in the m-dinitro benzenes **5a** to **8a**

Signal code	δ (ppm)	J_{cc} (Hz)	rel. intensities (%)
A, singlet	119.4	–	46.5
B, doublet	119.4	69 (^1J)	53.0
C, doublet	119.4	7 (^3J)	0.5

^{13}C-NMR Analysis of the Toluene Fraction

After the separation of the toluene from the liquid pyrolyzate, its ^1H-noise-decoupled ^{13}C-NMR spectrum was directly recorded and the chemical shifts compared with those obtained from corresponding NMR spectrum of the unlabeled toluene as well as with those published in ref. [7]. The proton-decoupled ^{13}C-NMR spectrum reveals the signals, which are listed in Table 4, together

Table 4 NMR signals of ^{13}C-atoms in the positions 1 to 5 of the doubly ^{13}C-enriched toluene fraction. Code numbers for different C-positions of toluene:

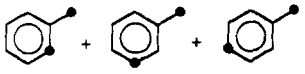
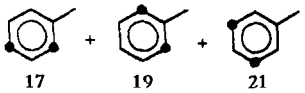
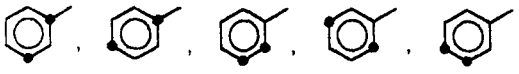


type of signal	δ (ppm)	J_{cc} (Hz)	rel. intensities (%)	position
doublet	21.3	45 (^{1}J)	27	1
singlet	21.3	–	2	1
singlet	125.9	–	4	5
doublet	128.5	79 (^{1}J)	6	3
singlet	128.8	–	15	4
singlet	128.5	–	14	3
doublet (2x)	137.5	45; 79 (^{1}J)	32	2

with their relative intensities and the positions of the ^{13}C-atoms from which the signals are derived. The interpretation of the NMR spectra is based on the above mentioned coupling constants for aromatic C-atoms in ortho-, meta- and para-position [6] as well as already published chemical shifts [7].

The signals of the ^{13}C-atoms in position 4 and 5 are found to be singlets. In the case of the isotopomers **16** and **20** there is another ^{13}C-atom in ortho-position which gives rise to an ortho-coupling constant of $^1J_{cc} \approx 60$ Hz. Both isotopomers are available in the toluene to less than 1 %. The isotopomers **14** and **15** contribute to the toluene fraction in a similarly small portion because the signal for the C-atom in position 2 shows two doublets only but no singlet. This leads to the conclusion that the ^{13}C-atom in position 2 must essentially have an additional ^{13}C in ortho position as is the case in **9** and **13**. The ratio of the integrated areas for the ^{13}C-atoms in the positions 1, 2 and 3 was determined to be 130 : 158 : 30. That gives a ratio of **9** : **13** of 130 : 30. The intensities of the singlet and the doublet for the ^{13}C in the position 1 give information about the ratio of the availability of the isotopomers of **9** to the sum of **10**, **11** and **12**, which comes up to 13 : 1. By analogy of that the signal intensities for the singlet and the doublet of the ^{13}C in position 3 gave a ratio of **13** to the sum of **10**, **17** and 0.5 × **19** of 30 : 68. In the isotopomer **18** the ^{13}C-atoms are situated in the para-position. From the literature, there is to be expected a para-coupling constant of about 7 Hz [6]. Such a coupling constant could not, however, be observed. This means that the isotopomer **18** can not be present in amounts larger than 1 %, if at all. The composition of the doubly ^{13}C-labeled toluene isotopomers resulting from the above described explanations are demonstrated in Table 5.

Table 5 composition of the [$^{13}C_2$]toluenes

[$^{13}C_2$]toluene isotopomers	portions of the total toluenes (%)
 **9**	53
 **10** **11** **12**	4
 **13**	12
 **17** **19** **21**	30
 **14** **15** **16** **18** **20**	traces

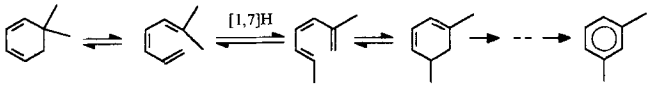
Discussion

Our recent results confirm in an impressive manner formerly published observations [2] according to which C-atoms of alkyl groups in α-position to 1,3-cyclohexadienes can be integrated partially in the ring system of the resulting aromatics during pyrolysis, and they clearly reveal that the C-atoms of methyl groups interchange positions with the original ring C-atoms of the 1,3-cyclohexadiene system in a much more complicated way than it was presumed hitherto. The fact that cross experiments with mixtures of unlabeled and doubly ^{13}C-labeled methyl-1,3-cyclohexadienes showed no C-disproportionation [4] is to be considered a strong argument for the presumption that the C-ensemble of the methyl-1,3-cyclohexadienes stays together during its conversion to aromatic hydrocarbons with the same number of C-atoms. The fact that doubly ^{13}C-labeled methyl-1,3-cyclohexadienes convert predominantly to the toluene isotopomer **9** (53 %) implies that the aromatization process must involve a doubly radical hydrogen abstraction of the starting compounds **1** to **3**. This conclusion remains valid even if more than 40 % of starting compounds interchange C-atom positions between the methyl group and the ring system in a hitherto not interpretable way.

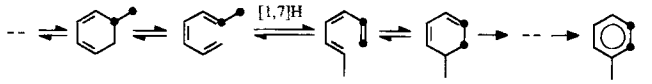
The toluene isotopomers **13**, **17**, **19** and **21** represent compounds, in which the orginal methyl C-atom of the methyl-1,3-cyclohexadienes is integrated in the six-membered C-ensemble of the aromatic 6 π-system.

According to the relevant literature such an integration of the methyl C-atom into the aromatic ring system could be the result of a preceding interconversion of the

methylcyclohexadienes as it was first suggested by Pines and Kozlowski [8] in the framework of the thermal conversion of 5,5-dimethyl-1,3-cyclohexadiene to m-xylene at 300 to 500 °C. The essential step of this interpretation includes a sigmatropic 1,7-H shift of 1,3,5-heptatrienes as is demonstrated in Scheme 4.



A preceding electrocyclic ring opening of the 5-methyl-1,3-cyclohexadiene and a consecutive recyclization should be embedding the [1,7]H shifts. Sigmatropic 1,7-H shifts were also brought into discussion to explain the results of the thermal conversion of other cyclic [9–13] and acyclic oligoenes [14]. Meanwhile, the reaction sequence consisting of the electrocyclic opening of the alkyl-1,3-cyclohexadienes, a [1,7]H shift reaction of the formed 1,3,5-alkatrienes and their recyclization to alkyl-1,3-cyclohexadienes represents a prime example of sigmatropic [1,7]H shifts [15]. If the integration of methyl C-atoms into the aromatic ring system via such a sequence were an important route from methyl-1,3-cyclohexadienes to toluene, the formation of the toluene isotopomer **16** ([2,3-$^{13}C_2$]methylbenzene) had to be formed to a significant extent (Scheme 5).



16 is formed, however, only in traces, if at all. This result shows clearly that the aromatization of methyl-1,3-cyclohexadienes to toluene is thought to occur via other mechanistic routes, which are widely unknown up to now. The only one which can be taken as certain is the statement that the observed C-scrambling doesn't take place in a disordered manner. The quantification of the established isotopomers and the fact that the existence of some imaginable ones that could not be established demonstrate clearly that the reaction course obviously follows certain, but in the end, still unknown rules. In this context it seems to be of some importance that the comparison of the ^{13}C-distribution patterns in the aromatic ring systems of the formed benzene and toluene (Table 6) results in far-reaching similarities. These findings suggest the conclusion that the future structure of aromatic rings is already established before the decision about the alternative cleavage of a methyl group or an H-atom is taken.

Conclusions

It has been demonstrated that the C-atoms of methyl-1,3-cyclohexadienes interchange methyl group and ring C-positions during the thermal conversion to toluene and benzene at temperatures above 600 °C in a quartz flow system. The experimental results support former observations about the integration of methyl C-atoms into the aromatic 6 π-systems of toluene and benzene [2]. The data reveal clearly that a reaction sequence via electrocyclic ring opening of methyl-1,3-cyclohexadienes to 1,3,5-heptatrienes, [1,7]shift reactions and ensuing recyclization to methyl-1,3-cyclohexadienes with interchanged positions of the C-atoms do not play an important role in the integration of the methyl C-atoms of the starting cyclohexadienes into the toluene ring system.

None of the several hitherto published mechanisms that could explain the radical formation of toluene from methyl-1,3-cyclohexadienes are able to give a convincing interpretation of the observed pattern ot the toluene isotopomers.

Table 6 ^{13}C-distribution in the aromatic ring systems of benzene and toluene

number of ^{13}C-atoms	position	benzene	toluene
1	–	43	57
2	ortho	24	12
	meta	33	30
	para	1	< 1

We thank the Volkswagenstiftung and the Fonds der Chemischen Industrie for their support of our work. For numerous structure determinations by NMR spectroscopy we are particularly grateful to Dr. Matthias Findeisen.

Experimental

^{13}C-NMR (c-C_6D_{12} (for toluene), $CDCl_3$ (for benzene), int. HMDSO): BRUKER AM 250 at 62.9 MHz, invers gated ^{1}H-noise-decoupled. – GC (analytic, gaseous products): CHROMATRON GCHF 18.3 (6-m packed stainless-steel columns Al_2O_3, PPN and ODPN at Porasil); GC (total analysis): VARIAN 1740 (50-m glas capillary, SE-30, H_2); GC (preparative): self-made set-up based on a CHROMATRON GCHF 18.2 (6-m packed stainless-steel column, SE-30, H_2). – GC-MS: HP5890 serie II (50-m glas capillary, SE-54)/HP 5971A.

Preparation of the Methyl-1,3-cyclohexadienes

The unlabeled methyl-1,3-cyclohexadienes were synthesized by the procedure described for the [methyl, ring-$^{13}C_2$]-labeled ones. The specification was optimized using unlabeled compounds with respect to the expenditure of NaCN and CH_3I, respectively.

The synthesis of the mixture of [methyl, ring-$^{13}C_2$]methyl-1,3-cyclohexadienes isomers was carried out starting from 1,5-dibromopentane and Na^{13}CN and passing [cyano-$^{13}C_2$]-1,5-dicyanopentane, [carboxyl-$^{13}C_2$]pimelic acid, [carbonyl-^{13}C]cyclohexanone, [methyl, ring$^{13}C_2$]methylcyclohexanol, [methyl, ring-$^{13}C_2$]-1-methyl-cyclohexene and [methyl, ring-$^{13}C_2$]-1,2-dibromo-1-methylcyclohexane as reaction intermediates and resulting in a mixture of the corresponding [$^{13}C_2$]-1-methyl-, [$^{13}C_2$]-2-methyl- and [$^{13}C_2$]-5-methyl-1,3-cyclohexadiene, and [$^{13}C_2$]-3-methylene cyclohexene.

[Cyano-$^{13}C_2$]-1,5-dicyanopentane (= 1,7-^{13}C-enriched pimelonitrile) was prepared by the reaction of 1,5-dibromopentane (13.1 g, 57 mmol) with $Na^{13}CN$ (8 g, 123 mmol; 99.5 atom percent ^{13}C) in a water-ethanol mixture at 80 °C (25 h) using catalytic amounts of potassium iodide as described in ref. [16]. The yield and the boiling point confirme with that given in ref. [16] for the unlabeled compound (yield of the crude product 95 % of theory referred to $Na^{13}CN$).

[Carboxyl-$^{13}C_2$]pimelic acid was received by analogy to ref. [17] from the crude [$^{13}C_2$]-pimelonitrile (6.7 g, 54 mmol) by hydrolysis by means of a surplus of a concentrated solution of caustic soda (5 h under reflux), followed by neutralization of the resulting reaction mixture, extraction of the remainder of unconverted dinitrile with chloroform and precipitation of the corresponding pimelic acid by acidification with half-concentrated hydrochloric acid (m.p. 102–104 °C (ref. [18]: 103–105 °C), yield 85 % of theory).

[Carbonyl-^{13}C]cyclohexanone, prepared in analogy to ref. [19, 20], was received from the thoric salt of the pimelic acid and thermally decomposed at 350 °C. The formed [^{13}C]cyclohexanone was condensed and fractionated (b.p. 155 °C [20], yield 70 % of theory, GC purity >99 %). The released, ^{13}C-enriched CO_2 was precipitated as barium carbonate and used for other synthesis.

[Methyl, ring-$^{13}C_2$]-1-methylcyclohexanol [21]. The [^{13}C]cyclohexanone (3.2 g, 32 mmol) was dropped into a boiling mixture of the Grignard compound of ^{13}C-methyliodide (32 mmol, 99.5 atom percent ^{13}C) in ether, the formed alcohol isolated and directly used for the dehydration to the corresponding [$^{13}C_2$]-1-methylcyclohexene (yield 80 % of theory).

[Methyl, ring-$^{13}C_2$]-1-methylcyclohexene. The dehydration of the [$^{13}C_2$]-1-methylcyclohexanol (2.9 g, 25 mmol) was carried out by means of potassium hydrogensulfate following ref. [19, 22]. A mixture of the alcohol and 0.5 g of $KHSO_4$ was heated at 130 °C and the 1-methylcyclohexene, formed continously and was distilled off. The fractionation of the crude 1-methylcyclohexene contains the title compound with a GC purity of 98 % (b.p. 111 °C, yield 85 % of theory).

[Methyl, ring-$^{13}C_2$]-1,2-dibromo-1-methylcyclohexane (see, ref. [19, 23]. 2.1 g (21 mmol) of the precedingly described olefin was dissolved in 15 ml chloroform and then added drop by drop with 3.4 g (21 mmol) bromine. After removing the solvent the corresponding crude dibromide stays behind (yield 98 % of theory).

[Methyl, ring-$^{13}C_2$]methyl-1,3-cyclohexadienes [23]. The crude dibromide (5.1 g, 20 mmol) was added drop by drop to a boiling solution of sodium ethanolate in ethanol, and the mixture refluxed for about 30 minutes. After the mixture was cooled down to room temperature the precipitated sodium bromide was separated from the solution and the solvent distilled off. The remainder of the ethanol was removed by the addition of n-pentane and repeated extraction with water. After the pentane was distilled off the residual mixture of four C_7H_{10}-isomers was purified by means of preparative GC. The composition of the purified fraction is listed in Table 1. It was directly used as a feedstock for pyrolysis experiments (yield 0.75 g, corresponding to 40 % of theory of the converted crude dibromide.

Preparation of Authentic Methylfulvenes

6-Methylfulvene. Freshly distilled cyclopentadiene and acetaldehyde were converted in an ethanolic solution of sodium ethanolate at 10 °C as it is described by Thiele [24].

After treatment with ice-water the 6-methylfulvene was extracted with n-pentane and the pentanic solution directly used for the identification of product components by GC-MS.

2- and 3-Methylfulvene. Both the methylfulvenes were formed by pyrolysis (670 °C, $n_{N2} : n_{HC} = 50 : 1$) of 1,5-heptadiyne (commercial product). The pyrolyzate, consisting of a 35:35:30 mixture of 2- and 3-methylfulvene and toluene, was dissolved in n-pentane.

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