BIRADICAL INTERMEDIATES IN 7.6 eV PHOTON-INDUCED ISOMERIZATION OF LIQUID ALKYLCYCLOHEXANES

L. WOJNÁROVITS, L. KOZÁRI, CS. KESZEI and G. FÖLDIÁK

Institute of Isotopes of the Hungarian Academy of Sciences, H-1525 Budapest, P.O. Box 77 (Hungary)

Summary

Structural isomerization to open-chain alkenes was observed in the photolysis of methylcyclohexane, 1,2-dimethylcyclohexane, 1,3-dimethylcyclohexane and 1,4-dimethylcyclohexane; *cis–trans* geometrical isomerization was also found in the dimethylcyclohexanes. The results of deuterium labelling experiments on methylcyclohexane and examinations of the product distributions suggest that biradicals are intermediates of both types of isomerization. The lifetime of the biradical state is assumed to be a few times the rotation time around a C—C bond.
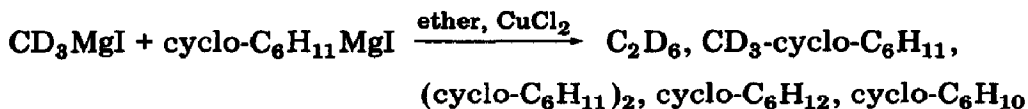
1. Introduction

During the liquid phase γ radiolysis of alkylcyclopentanes and alkylcyclohexanes 10% - 30% of the total transformation involves unimolecular isomerization to straight-chain alkenes [1 - 3]. This isomerization is assumed to occur through excited molecules, although under radiolytic conditions ionic isomerization reactions may also take place. The latter processes are disclosed when the reactions are carried out using photons with energies slightly above those required to initiate vacuum UV absorption (6.7 - 7.3 eV) and well below the ionization potentials (about 10 eV [4]). In this work we investigated the isomerization of several liquid alkylcyclohexanes by 7.6 eV photons from a bromine lamp. Under these conditions the reactions probably proceed through the first singlet excited state S_1 of the molecules and, according to general experience [5 - 7], the transformations are mostly monomolecular with some contribution from radical bimolecular reactions.

2. Experimental details

The hydrocarbons (methylcyclohexane (MCH) and dimethylcyclohexanes (DMCHs) (Fluka)) were purified by treatment with sulphuric acid, distillation and preparative gas chromatography to decrease the percentage

of hydrocarbon impurities below 0.05%. 1,3-DMCH was available only in the form of the *cis–trans* mixture, and these isomers were separated by preparative gas chromatography. (Methyl-7,7,7-d_3)-cyclohexane (MCH-d_3) was synthesized in our laboratory via the Grignard compounds of methyl-d_3 iodide (VEB Berlin-Chemie, isotopic purity 99.7%) and cyclohexyl iodide (Fluka):

$$CD_3MgI + cyclo\text{-}C_6H_{11}MgI \xrightarrow{\text{ether, } CuCl_2} C_2D_6, CD_3\text{-}cyclo\text{-}C_6H_{11},$$

$$(cyclo\text{-}C_6H_{11})_2, cyclo\text{-}C_6H_{12}, cyclo\text{-}C_6H_{10}$$

The mixture formed in this reaction was distilled and MCH-d_3 with a purity of about 99% was obtained from the mid-fraction by preparative gas chromatography. For identification purposes we prepared 1,1,1-d_3-2-heptene via the 1-bromo-1-hexene Grignard compound.

The oxygen, carbon dioxide and water dissolved in the samples were removed by the freeze–pump–thaw technique and by storing the samples on a sodium mirror prior to irradiation. The irradiations were carried out in the liquid phase at 25 ± 3 °C with equipment similar to that described in refs. 7 and 8. The liquid covered the Suprasil quartz lamp window completely, and the samples were stirred during photolysis. The quantum intensity of the lamp was 8×10^{15} s^{-1} and the irradiation times of the 6 ml samples varied from 40 to 80 min. As in refs. 7 and 8 the discharge was powered by a stabilized microwave generator and the lamp output in one series of experiments (lasting for several hours) did not change more than ±3% - 4%. The actinometry was based on the molecular hydrogen yield of pure cyclohexane taking the quantum yield as unity [7, 8]. The hydrogen formation was measured by the Toepler method, and in most cases the hydrocarbon products were analysed by capillary gas chromatography. The mass spectra of the products were obtained with a Du Pont 21-490B gas chromatography–mass spectroscopy system (electron energy 70 eV) in which the separation was carried out using a squalane-coated column 1.5 m long.

3. Results

The experimental results are summarized in Tables 1 - 5.

3.1. Isomerization of methylcyclohexane

The 1-heptene and 2-heptene products formed from MCH (Table 1) suggest that the ring opens at the tertiary carbon atom (Fig. 1, structure I). The migration of a hydrogen atom is necessary for the formation of the final products. If the migrating hydrogen atom originates from a carbon atom attached to one of the carbon atoms of the breaking bond there are three possible routes for end-product formation. These are shown in the scheme in Fig. 2 according to which we expect 1-heptene-7,7,7-d_3
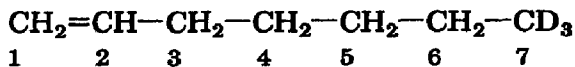
$$\begin{array}{ccccccc} CH_2 & = CH & -CH_2 & -CH_2 & -CH_2 & -CH_2 & -CD_3 \\ 1 & 2 & 3 & 4 & 5 & 6 & 7 \end{array}$$

TABLE 1

Quantum yields of ring-opening products from methylcyclohexane and (methyl-7,7,7-d_3)-cyclohexane

Ring-opening behaviour[a]	Type of rearrangement[b]	Product	Quantum yield	
			MCH	MCH-d_3
I	(a), (c)	1-heptene	0.07	0.067
	(b)	trans-2-heptene	0.022	0.028
		cis-2-heptene	0.010	0.012

[a] See Fig. 1.
[b] See Fig. 2.

TABLE 2

Quantum yields of ring-opening products from 1,2-dimethylcyclohexanes

Ring-opening behaviour[a]	Type of rearrangement[b]	Product	Quantum yield	
			cis-1,2-DMCH	trans-1,2-DMCH
IIa	(a), (b)	trans-2-octene	0.193	0.251
		cis-2-octene	0.084	0.052
	(c)	1-octene	0.051	0.046
IIb	(a)	5-methyl-1-heptene	0.004	0.007
	(b)	trans-3-methyl-2-heptene	0.024	0.021
		cis-3-methyl-2-heptene	0.010	0.016
	(c)	3-methyl-1-heptene	0.004	0.002

[a] See Fig. 1.
[b] See Fig. 2.

TABLE 3

Quantum yields of ring-opening products from 1,3-dimethylcyclohexanes

Ring-opening behaviour[a]	Type of rearrangement[b]	Product	Quantum yield	
			cis-1,3-DMCH	trans-1,3-DMCH
IIIa	(a)	2-methyl-1-heptene	0.003	Trace
	(b)	trans-6-methyl-2-heptene	0.011	0.007
		cis-6-methyl-2-heptene	0.004	0.007
	(c)	6-methyl-1-heptene	Trace	0.004
IIIb	(a), (c)	4-methyl-1-heptene	0.029	0.025
	(b)	trans-4-methyl-2-heptene	0.046	0.039
		cis-4-methyl-2-heptene	0.011	0.014

[a] See Fig. 1.
[b] See Fig. 2.

TABLE 4

Quantum yields of ring-opening products from 1,4-dimethylcyclohexanes

Ring-opening behaviour[a]	Type of rearrangement[b]	Product	Quantum yield	
			cis-1,4-DMCH	trans-1,4-DMCH
IV	(a)	3-methyl-1-heptene	0.049	0.057
	(b)	{ trans-5-methyl-2-heptene	0.042	0.054
		{ cis-5-methyl-2-heptene	0.037	0.024
	(c)	5-methyl-1-heptene	0.034	0.031

[a] See Fig. 1.
[b] See Fig. 2.

TABLE 5

Summarized quantum yields from alkylcyclohexane transformations

| Product	MCH	MCH-d_3	1,2-DMCH		1,3-DMCH		1,4-DMCH	
			cis	trans	cis	trans	cis	trans
1 Hydrogen	0.77	0.73	0.46	0.39	0.59	0.66	0.61	0.56
2 Ring-opening products	0.102	0.107	0.37	0.39	0.10	0.10	0.16	0.17
3 Other products[a]	0.03	0.03	≈ 0.01	≈ 0.01	≈ 0.02	≈ 0.02	≈ 0.02	≈ 0.02
4 Geometrical isomerization	—	—	0.12	0.07	0.07	0.15	0.13	0.06
$\Sigma(1 - 4)$	0.90	0.87	0.96	0.86	0.78	0.93	0.92	0.81
$1 - \Sigma(1 - 4)$	0.10	0.13	0.04	0.14	0.22	0.07	0.08	0.19

[a] Includes side-chain elimination and eventually ring fragmentation.
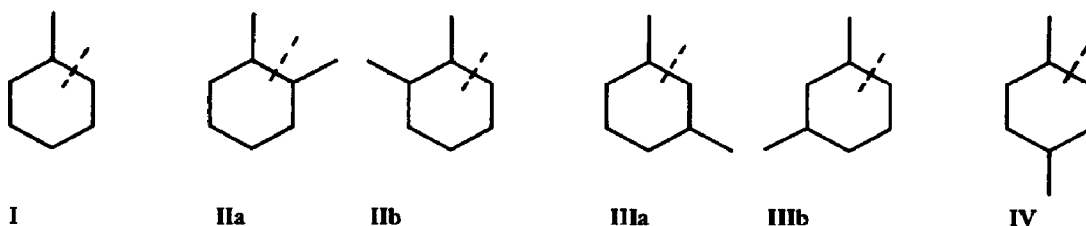
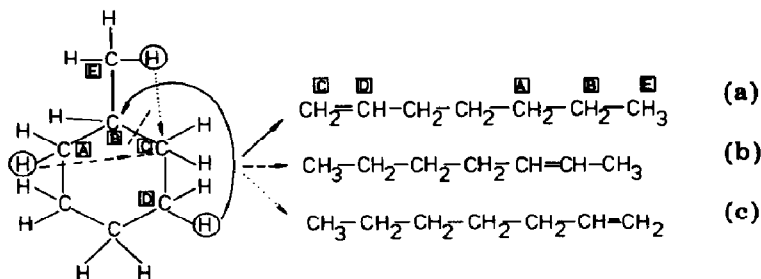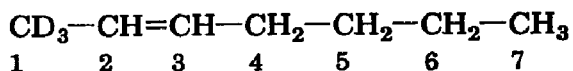Fig. 1. Ring-opening behaviour of alkylcyclohexanes.

and 1-heptene-1,1,7-d_3

$$CD_2{=}CH{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2D$$
$$1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6 \quad 7$$
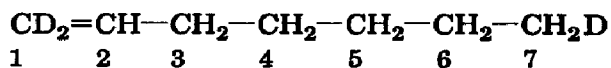
Fig. 2. Scheme of the different types of rearrangement.

to be formed from MCH-d_3 in reactions (a) and (c) respectively, whereas the 2-heptene (reaction (b)) is expected to contain the deuterium atoms in the 1,1,1 position:

$$CD_3—CH=CH—CH_2—CH_2—CH_2—CH_3$$
$$1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6 \quad 7$$

The mass spectra of the unlabelled and labelled heptenes are shown in Fig. 3 for m/e in the range 27 - 73.

Many data have been accumulated on the fragmentation patterns of alkene ions [9 - 12], and these are a great help in our identifications. For instance, Falick and Gäumann [11], by detailed ^{13}C and D labelling studies
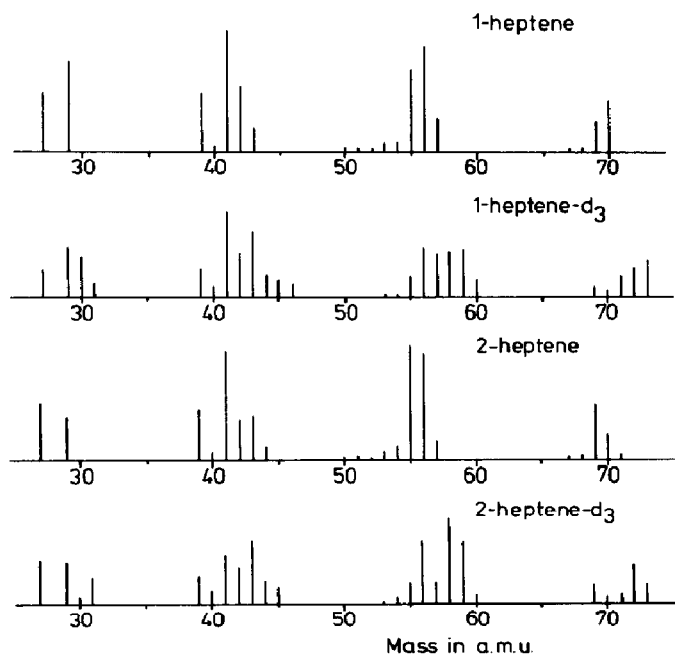

Fig. 3. Mass spectra of heptenes for m/e in the range 27 - 73. Masses 28 and 32 are excluded because of the presence of nitrogen and oxygen impurities.

on 1-heptene fragmentation, demonstrated that the ethylene loss occurs primarily from the unsaturated end of the molecule. On the basis of this result, if the 1-heptene-d_3 produced from MCH-d_3 contains 1-heptene-7,7,7-d_3, a relatively intense peak corresponding to $C_5H_7D_3^+$ should occur at m/e = 73, in accordance with the recorded spectra. By a similar fragmentation process 1-heptene-1,1,7-d_3 should produce a peak at m/e = 71 corresponding to $C_5H_9D^+$.

The allylic cleavage of the 1-heptene ion with charge retention on the heavier part leads to a $C_4H_9^+$ fragment (m/e = 57); the analogous process from 1-heptene-7,7,7-d_3 must be principally responsible for the peak at m/e = 60 corresponding to $C_4H_6D_3^+$. Some characteristics of the 1-heptene-d_3 spectrum also provide evidence for the formation of 1-heptene-1,1,7-d_3. For instance, we expect a relatively weak peak at m/e = 57 if only 1-heptene-7,7,7-d_3 is present, in disagreement with the recorded spectrum. However, on the basis of literature data [11] this peak should be one of the most intense in the spectrum of 1-heptene-1,1,7-d_3. If the 1-heptene-d_3 spectrum in Fig. 3 is really composed of the spectra of the 7,7,7-d_3 and 1,1,7-d_3 isomers, it is certain that the proportion of the former is higher than that of the latter. (In agreement with this result, capillary chromatography of 1-heptene-d_3 demonstrated a separation into two overlapping peaks with an approximate area ratio of 1:3.)

The mass spectrum of 2-heptene-d_3 produced from MCH-d_3 is in good agreement with that of the synthetic 2-heptene-d_3. We also found that, on separating the photolysis products by squalane capillary chromatography, the Kováts retention indexes of the *trans* and *cis* isomers of 2-heptene-d_3 (698.0 and 702.6 respectively at 27 °C) agreed with those of the synthetic compounds and were slightly different from those of the undeuterated 2-heptenes (699.2 and 703.2).

In conclusion, our labelling experiments support the assumption that the rearrangement occurs according to the scheme in Fig. 2.

3.2. Experimental observations regarding the isomerization of alkylcyclohexanes

During our experiments we made the following observations.

(1) Isomerization to open-chain alkenes took place in the photolysis of all the alkylcyclohexanes studied (Tables 1 - 4). The distribution of the products corresponded to the scheme in Fig. 2. The alkenes contained a double bond between one pair of carbon atoms, one of which participated in the C—C bond rupture in the ring: (a) all variations of these alkenes (including the *cis* and *trans* isomers) were produced, and (b) no other open-chain alkenes were observed.

(2) The hydrogen atom migration needed to produce the alkenes presumably occurs in the way shown in the scheme.

(3) Experiments were carried out with MCH in the presence of radical acceptors such as iodine or oxygen, the latter being also a scavenger of triplet states. No substantial reductions in the yields of the open-chain alkenes were

observed, indicating that long-lived radicals and triplet states have at most a minor role in the formation of these products.

(4) The proportions of (a) and (b) type rearrangements are usually higher than that of (c) (Fig. 2).

(5) The percentage distributions of alkenes produced from the *cis* and *trans* DMCHs show substantial differences. The *cis*-to-*trans* ratio for the 2-alkenes is higher in the photolysis of the less stable isomer (*cis*-1,2-, *trans*-1,3- and *cis*-1,4-) than in the transformation of the corresponding more stable isomer (*trans*-1,2-, *cis*-1,3- and *trans*-1,4-).

(6) Geometrical isomerization, *i.e.* the production of the *trans* isomer from the *cis* isomer and vice versa, was also observed in the photolysis of 1,2-DMCH, 1,3-DMCH and 1,4-DMCH. In all cases, however, the production of the more stable isomer from the less stable isomer had a higher yield than the reverse process.

Table 5 shows that the overall quantum yield $\Sigma(1 - 4)$ of hydrogen, the ring-opening products, the geometrical isomers and the products of lower yield is less than unity for all the compounds investigated, although in several cases the difference is of the order of the experimental error ($\pm 8\%$). The deficit is higher for the more stable geometrical isomers of the DMCHs than for the less stable isomers.

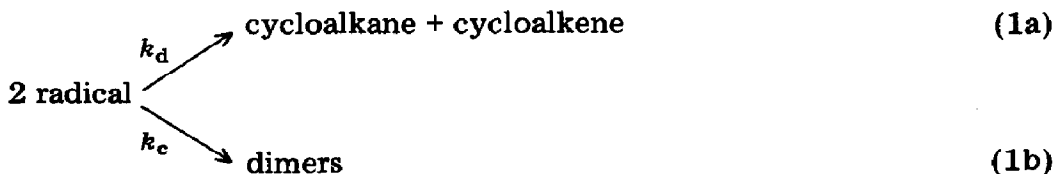## 4. Discussion

4.1. Mechanism of isomerization

Two fundamentally different reaction mechanisms have been proposed in the literature [13 - 15] for isomerization reactions similar to those observed in our work: these are the concerted and the biradical pathways. If a concerted mechanism is assumed for the formation of open-chain alkenes, the hydrogen atom migration will occur before or during the C—C bond rupture. However, if the biradical mechanism is assumed, the C—C bond rupture occurs first resulting in the formation of a biradical that, at least in principle, has a bifunctional character. The product alkene is then formed by internal hydrogen atom migration. In biradical reactions the parallel formation of several products is usually observed, whereas the concerted processes are highly stereospecific and yield one or a very limited number of products. The large number and the wide distribution of products found in the present work (Section 3.2, observations 1 - 3) suggest a biradical mechanism.

It was found that the material balance shows a deficit (Section 3.2, observation 6). The deficit cannot be caused by fluorescence because its yield is very low in the photolysis of alkanes ($\Phi_f \leqslant 0.01$) [16]. At the same time, the fact that the primary decomposition of numerous alkanes occurs with a quantum yield close to unity [5 - 7, 17] is evidence for the negligible importance of energy loss processes involving no chemical decomposition ($S_1 \rightarrow S_0$ transition with the excess energy dissipating over the vibrational levels).
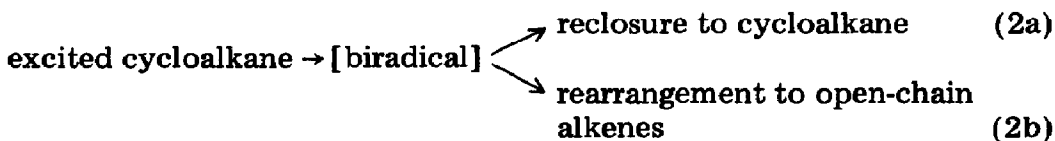
It appears reasonable to assume that the deficit is caused by inter-
mediates that re-form the parent hydrocarbon in their subsequent reactions
and therefore cannot be observed by our technique. It is worth noting that
in the photolysis of the more stable geometrical DMCH isomers the yield of
re-formation is higher than that of geometrical isomerization. In the photol-
ysis of the less stable isomers the reverse is the case: the yield of geometrical
isomerization exceeds that of re-formation. This means that in both cases
the more stable isomer forms from the intermediate at a higher rate than the
less stable isomer does.

There are three reaction possibilities for re-formation and geometrical
isomerization: (a) the elimination of a methyl radical followed by recombina-
tion; (b) the elimination of a hydrogen atom from any of the tertiary
carbons followed by disproportionation of the monoradical to give the
alkane again; (c) ring opening to a biradical followed by reclosure.

Since the methane yield was found to be very low ($\Phi \leqslant 0.01$) for the
compounds investigated, possibility (a) can be ignored. The yield of tertiary
alkyl radicals produced as a consequence of atomic hydrogen formation is
presumably low, as is suggested by the low dimer yield ($\Phi = 0.01 - 0.04$).
If the ratio k_d/k_c of the radicals formed in the photolysis is assumed to be
approximately 3 [18],

$$2 \text{ radical} \begin{array}{c} \overset{k_d}{\nearrow} \text{cycloalkane + cycloalkene} \qquad \text{(1a)} \\ \\ \underset{k_c}{\searrow} \text{dimers} \qquad \text{(1b)} \end{array}$$

the maximum quantum yield of re-formation and cyclic isomerization in
reaction (1a) is about 0.05 - 0.1 which is less than half the value actually
observed. In view of this, it can be assumed that re-formation and cyclic
isomerization also occur, at least partly, via the biradicals:

$$\text{excited cycloalkane} \rightarrow [\text{biradical}] \begin{array}{c} \nearrow \text{reclosure to cycloalkane} \qquad \text{(2a)} \\ \\ \searrow \text{rearrangement to open-chain} \\ \text{alkenes} \qquad \text{(2b)} \end{array}$$

4.2. The nature of the intermediate biradicals

In structural isomerization (Fig. 2) reactions (a) and (b) involve a
1,5-hydrogen shift (as shown for the 1,4-DMCHs in Fig. 4) via a six-membered
activated complex, whereas for reaction (c) to proceed an eight-membered
cyclic complex is necessary (1,7-hydrogen atom migration). The considerable
strain in the eight-membered rings (about 42 kJ mol^{-1} [13]) may explain
the lower probability of reaction (c) compared with (a) and (b) (observa-
tion 4). In Fig. 4(b) the structural isomerization of cis-1,4-DMCH is shown
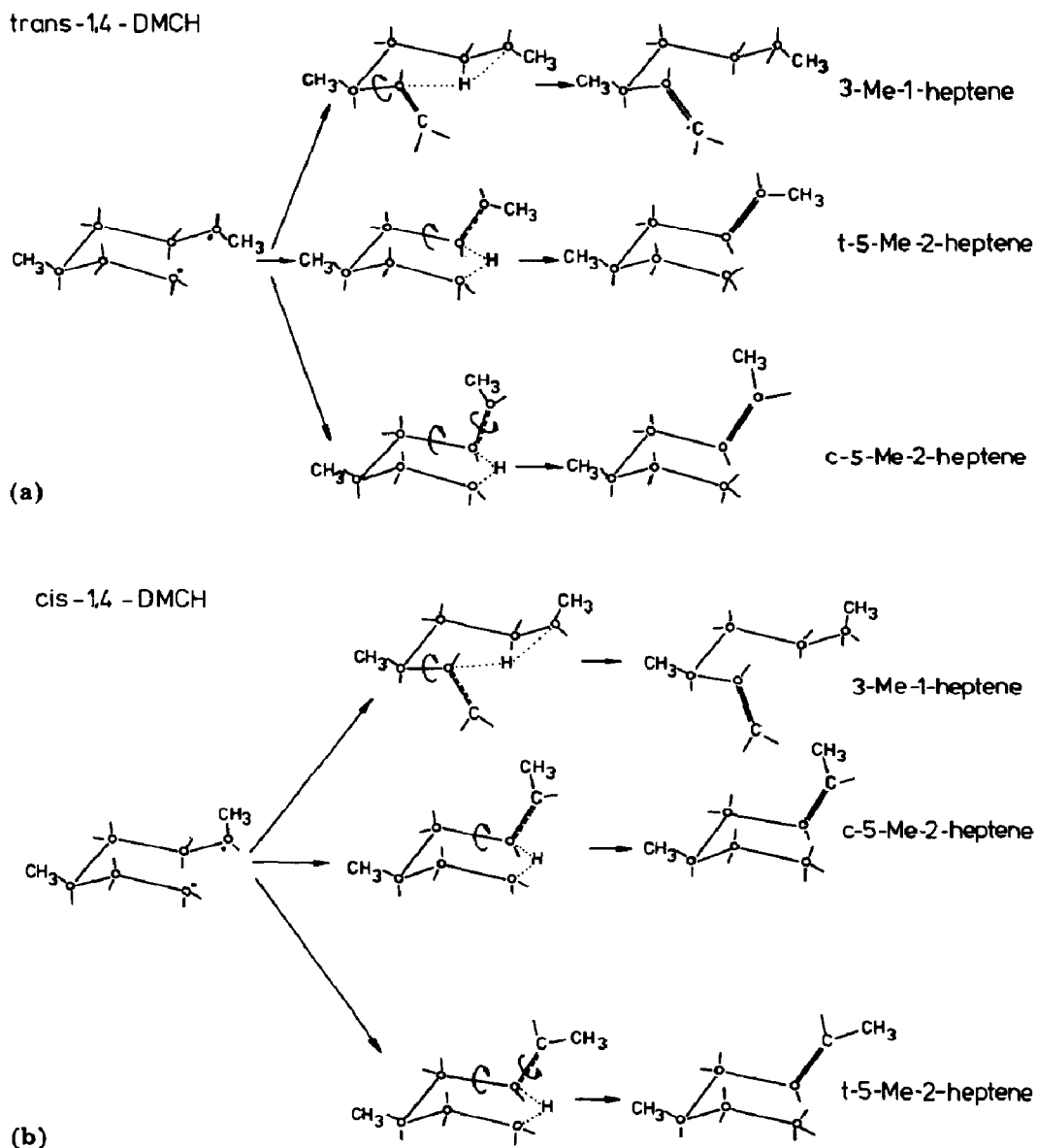with the ring cleavage occurring at the axial methyl group. The other case

Fig. 4. The structural isomerization of 1,4-DMCHs.

(cleavage at the equatorial methyl group) is practically the same as that of *trans*-1,4-DMCH as regards the development of the final products.

Since the C—H bond is shorter than the C—C bond, in the activated state for the 1,5-hydrogen shift the C—C· · ·H· · ·C—C system is close to a planar arrangement and the activated state is more reminiscent of an envelope conformation than a chair conformation (see ref. 15). Favourable transition states for a 1,5-hydrogen shift from the biradical can very easily be produced by rotations around the C—C bonds with subsequent slight distortions of the bond angle. It is obvious from Fig. 4(a) that less motion of the biradical

formed from *trans*-1,4-DMCH is required for transition states leading to 3-methyl-1-heptene and *trans*-5-methyl-2-heptene than to produce a transition state favourable for *cis*-5-methyl-2-heptene formation. In the case of *cis*-1,4-DMCH with ring scission at the axial methyl group less motion of the biradical is required to form *cis*-5-methyl-2-heptene than to form *trans*-5-methyl-2-heptene. This may explain why the *cis*-to-*trans* ratio of the alkenes is higher for those DMCH isomers that contain an axial methyl group, *i.e.* the less stable isomers (observation 5). This explanation implies a very short lifetime for the biradical state (not more than a few times the rotation time around a C—C bond, *i.e.* about 10^{-12} s). This means that the biradical produced prior to the formation of the activated complex leading to stable products does not "straighten out" completely but partially retains its original conformation.

Because the lifetime is presumably very short, singlet–triplet conversion of the intermediate biradical seems to be improbable [14], and thus it is reasonable to assume that the isomerization proceeds within the singlet manifold of states from the singlet excited state of the initial alkane to the ground singlet state of the final products.

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