JOURNAL OF CATALYSIS **81,** 405–417 (1983)

Isomerization and Cracking of ^{13}C-Labeled Hexanes over H-Mordenite

II. Intramolecular Rearrangements of the Hexyl Cations

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Received October 5, 1981; revised September 10, 1982

The intramolecular rearrangements of the branched hexyl cations which take place at 170°C over H-mordenite have been studied by using ^{13}C labeling techniques. Each individual step of these rearrangements including alkyl shifts (1,2-ethyl shift, 1,3-methyl shift, and 1,2-methyl shift), branching rearrangements (interconversions between the two methylpentanes and 2,3-dimethylbutane), and interchanges between internal and external carbon atoms has been isolated. Alkyl shifts proceed through alkyl bridged cations as transition states. Their relative rates are in the sequence: 1,2-ethyl shift > 1,3-methyl shift > 1,2-methyl shift. This result is interpreted by differences in the stabilities of the alkyl bridged structures. The branching rearrangements and the carbon interchange reaction are best explained by considering equilibration between corner- and edge-protonated alkyl cyclopropanes and alkyl bridged structures.

INTRODUCTION

Skeletal isomerization of branched hexanes readily takes place over H-mordenite at 170°C (*1*). When considering only the structure of the isomers formed, a very simple reaction model, involving interconversion between the two methylpentanes and 2,3-dimethylbutane, is obtained. However, when ^{13}C-labeled 3-methylpentanes are used as starting materials a somewhat more complicated situation is revealed. Besides the isomers which are expected by alkyl shifts or branching rearrangements (*2*), methylpentanes in which internal and external carbon atoms have been exchanged and molecules with a statistical distribution of the labels are also formed. Furthermore, depending on the conditions of the analysis, the respective percentages of these three types of products in the reaction mixture change significantly.

The formation of hexanes with a randomized ^{13}C distribution has been discussed in Part I (*1*). In this work the ^{13}C tracer technique has been used extensively to study the intramolecular rearrangements of the three tertiary hexanes.

The results obtained are presented in two main sections. In the first one we examine the labeling of the various reaction products and recovered reactants and isolate all the individual rearrangements. Each elementary step of these rearrangements is then considered in detail in the second section in order to understand better the factors which determine the reactivity of the intermediate cations.

EXPERIMENTAL

Reactions of ^{13}C-labeled branched hexanes were carried out at 170°C over 200 mg of H-mordenite. The catalyst, the flow system, the experimental, and the analytical

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0021-9517/83 $3.00

procedures have been described previously (*1*).

Selectively labeled methylpentanols and 2,3-dimethylbutanols were synthesized by the Grignard method (*3*). The starting materials were methyl[^{13}C]iodide, ethyl[1-^{13}C] iodide, [2-^{13}C]acetone, and ethyl[1-^{13}C]acetate from Merck Sharp and Dohme and had an isotopic purity of 90 or 60%. Labeled hydrocarbons were obtained by catalytic dehydration of the appropriate alcohol (*4*).

RESULTS AND DISCUSSION

Reaction mechanisms were studied with the following ^{13}C-labeled hydrocarbons: [1-^{13}C, 2-^{13}C, and 4-^{13}C]2-methylpentanes (2-MP-1-^{13}C, 2-MP-2-^{13}C, and 2-MP-4-^{13}C), [3-^{13}C]3-methylpentane and 3-methyl[^{13}C] pentane (3-MP-3-^{13}C and 3-M(^{13}C)P), and [1-^{13}C and 2-^{13}C]2,3-dimethylbutanes (2,3-DMB-1-^{13}C and 2,3-DMB-2-^{13}C).

The labeling of isobutane and isopentane, the main cracked products, has been already reported in Part I (*1*). The distribution of these hydrocarbons corresponds to a statistical association of ^{13}C and ^{12}C carbon atoms in the molecules (distribution C) and has been interpreted in terms of a polymerization–depolymerization process. In that work it was shown that part of the hexanes (up to 20%) could also be formed according to this mechanism, the remainder being associated with a true monomolecular isomerization reaction in which the original number of labels of the molecule is preserved (distribution I).

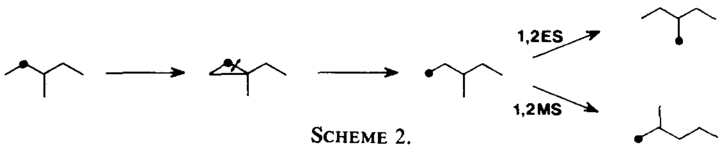
In order to obtain the location of the label in these latter molecules the contribution of the statistical distribution C was first determined from the labeling of the parent ions and subtracted from the total spectrum. Determination of the relative percentage of each isotopic variety was then effected as described earlier (*1*).

Labeling of the Hexanes

Reactions of 3-methylpentanes. The distributions of the monolabeled isomers obtained after reaction of [3-^{13}C]3-methylpentane and 3-methyl[^{13}C]pentane are given in Table 1. The major reaction product was an isotopic variety of 3-methylpentane resulting from a 1,2-ethyl shift (1,2-ES) (Scheme 1). (Since we are only interested in the labeling of the products in this section, positive charges will be omitted in the schemes.)

SCHEME 1.

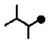
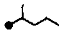
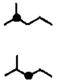
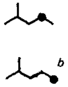
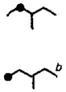
2-Methylpentanes which could result from a nonbranching rearrangement (1,2-methyl shift or 1,2-MS) of the starting and isomerized 3-MP were always formed in smaller amounts as shown by the values, larger than unity, of the ratio r_1 = 1,2-ES/1,2-MS. Among the methylpentane isomers, species which cannot be explained by single classical alkyl shifts (for example 2-MP-1-^{13}C and 3-M(^{13}C)P in runs 4 and 5) were detected in small quantities. Their formation corresponds formally to an interchange between internal and external carbon atoms followed by alkyl shifts (Scheme 2):



SCHEME 2.

TABLE 1

Isomerization of 3-Methylpentane: Distribution of the Monolabeled Species

Run number	Starting hydrocarbon	2,3-Dimethylbutanes			2-Methylpentanes				3-Methylpentanes				$r_1 = \frac{1,2\text{-ES}}{1,2\text{-MS}}$
		%[a]			%[a]			 [b]	%[a]		 [b]		
1		0.03	4.7	95.3	0.22	73.2	0.3	27.5	99.75	97.9	2	0.1	9.07
2		0.04	4.3	95.7	0.29	78.7	1	20.3	99.67	97	2.7	0.3	9.28
3		1.26	9.4	90.6	7.6	61.6	4	34.4	91.14	87.2	12.3	0.5	1.48
4		0.13	53.2	46.8	0.77	2	68.3	29.7	99.1	0.8	5.5	93.7	7.08
5		0.3	60	40	1.95	2.5	66.9	30.6	97.75	1	6.2	92.8	3.10
6	 [c]	2.65	60.9	39.1	11.24	0.2	71.4	28.4	86.11	—	16.7	83.3	1.28

[a] Percentages among the monolabeled isomers.

[b] Most probably in runs 1, 2, and 3.

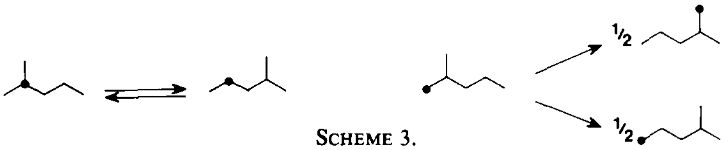
[c] Distribution of the products collected in the initial stages of the reaction.

The distribution of varieties in run 6, corresponding to an analysis of the products collected in the first stages of the reaction (*1*), recalls that these "abnormal" isomers are not observed initially even at relatively high conversion.

Besides 2-MP and 3-MP, 2,3-dimethylbutanes were also obtained. In the reaction of 3-M(^{13}C)P, 2,3-DMB-1-^{13}C was formed preferentially. In contrast, 2,3-DMB produced from 3-MP-3-^{13}C were extensively labeled on carbons 1 and 2.

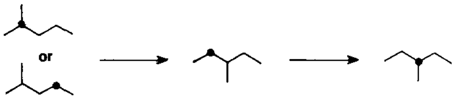
Reactions of 2-methylpentanes. The distribution of the monolabeled 2,3-DMB, 2-MP, and 3-MP formed in the reactions of 2-methylpentanes are listed in Table 2.

As already observed in the reactions of 3-MP, the major reaction products were isotopic isomers of the starting 2-methylpentanes. The isomerization process which accounts for their formation is a 1,3-methyl shift (1,3-MS) (*5*) (Scheme 3):



SCHEME 3.

The labeling of most 3-methylpentanes can be explained by a succession of a 1,2-MS and a 1,2-ES (Scheme 4):



SCHEME 4.

The ratio r_2 between the amounts of 2-methylpentanes formed by 1,3-methyl shift and the total percentages of 3-methylpentanes is listed in the last row of Table 2. r_2 is greater than 2 (except in run 10 made at high conversion) showing that 1,3-MS is faster than 1,2-MS.

"Abnormal" products, namely, 2-MP-1-^{13}C and 3-M(^{13}C)P in runs 7 to 10 and 2-MP-2-^{13}C or -3-^{13}C and 3-MP-3-^{13}C in runs 11 and 12, were again observed. These represented less than 7% of the total methylpentanes.

The distributions of the isotopic species of 2,3-DMB obtained from 2-MP-4-^{13}C (runs 7, 8) and 2-MP-2-^{13}C (runs 9, 10) were almost identical: 30% of the 2,3-dimethylbutanes were labeled on carbon 1 and 70% on carbon 2. In the reaction of 2-MP-1-^{13}C, 2,3-dimethylbutanes were exclusively labeled on position 1 at low conversion (run 11); at higher conversion (run 12) some 2,3-DMB-2-^{13}C was also formed.

Relative rates of the nonbranching rearrangements. In Fig. 1, the ratios r_2 = 1,3-MS/1,2-MS determined from the reactions of labeled 2-MP and r_1 = 1,2-ES/1,2-MS determined from the reactions of labeled 3-MP have been plotted versus isomerization conversion. The extrapolation of these curves to zero conversion, which allows an estimation of the relative rates of these migrations to be made, reveals that the rates

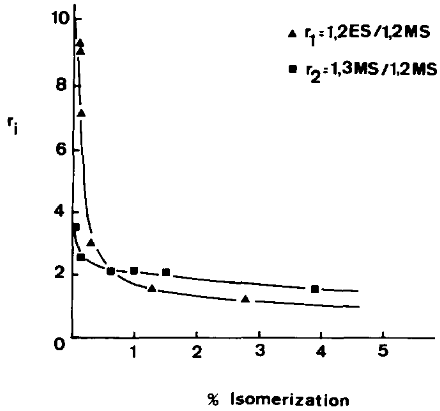
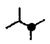
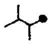
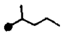
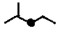
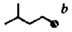
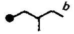
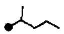
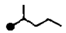


FIG. 1. Variations of the ratios r_1 = 1,2-ES/1,2-MS and r_2 = 1,3-MS/1; 2-MS as a function of isomerization conversion.

TABLE 2

Isomerization of 2-Methylpentane: Distribution of the Monolabeled Species

Run number	Starting hydrocarbon	2,3-Dimethylbutanes			2-Methylpentanes				3-Methylpentanes				$r_2 = \frac{1,3\text{-MS}}{1,2\text{-MS}}$
		%[a]			%[a]		 	 [b]	%[a]		[b] 		
7		0.13	67.8	32.2	99.25	0.2	1.6	98.2	0.62	2.5	78.8	18.7	2.56
8		1	67.7	32.3	96.93	2	4.7	95.1	2.07	0.3	72.8	26.9	2.20
9		0.62	69.4	30.6	97.81	0.6	96.4	3.6	1.57	6.2	71.8	22	2.24
10		3.82	73.6	26.4	90.78	0.3	89.5	10.2	5.40	4.3	71.3	24.4	1.71
11		0.07	0.4	99.6	99.35	98.9	0.1	1	0.58	26.8	71.4	1.8	3.45
12		1.58	12.8	87.2	95.68	96.5	0.3	3.2	2.74	30.7	65.8	3.5	2.33

[a] Percentages among the monolabeled isomers.

[b] Most probably in runs 11 and 12.

can be classified in the following sequence:

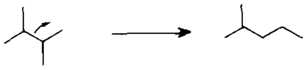
1,2-ES > 1,3-MS > 1,2-MS

with values of 10, 4, and 1, respectively.

Such a result, showing that the 1,2-ethyl shift is the fastest reaction in the rearrangements of branched hexanes, is similar to that already found on supported *p*-toluenesulfonic acid at 74°C (*5*) and on SbF_5-intercalated graphite at −17 and −30°C (*6*).

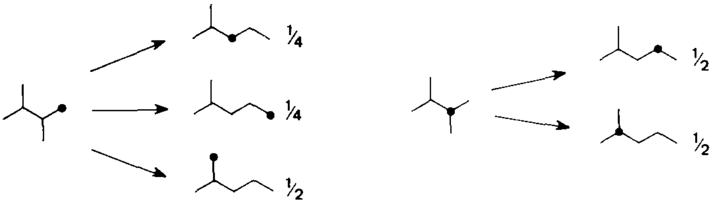
Reactions of 2,3-dimethylbutanes. The reactions of 2,3-DMB-1-^{13}C and -2-^{13}C gave the isotopic species listed in Table 3. Little redistribution of the label was found on the unreacted 2,3-DMB whereas a complex ^{13}C distribution, still far however from that associated to an equal distribution of the label on all six positions, was obtained in the methylpentanes.

The isotopic varieties of the 2-MP are best explained by assuming a formal 1,2-isopropyl shift (Scheme 5a):



SCHEME 5a.

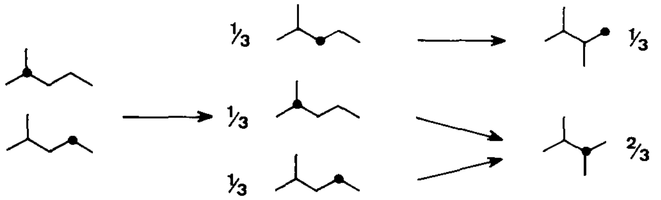
According to Scheme 5b, 2-MP-3-^{13}C, 2-MP-5-^{13}C, and 2-MP-1-^{13}C should be obtained in the ratio 1 : 1 : 2 in the reaction of 2,3-DMB-1-^{13}C and equal amounts of 2-MP-2-^{13}C and 2-MP-4-^{13}C should be formed in the reaction of 2,3-DMB-2-^{13}C.



SCHEME 5b.

As shown in Table 3 a very good agreement between the experimental and expected distribution is obtained in runs 13, 14, and 15. In run 16, some scrambling of the label (characterized by the formation of some 2-MP-1-^{13}C) occurred due to the higher conversion in this run.

The isopropyl shift allows us to explain also the identity of the distributions of the 2,3-DMB formed from 2-MP-2-^{13}C and 2-MP-4-^{13}C (runs 7 to 10, Table 2) if one considers that the slow branching rearrangement has been preceded by an equilibration of carbons 2, 3, and 4 in the 2-MP (Scheme 6):

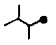
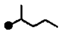
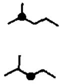
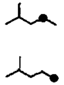
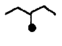
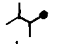
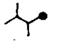
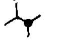
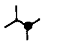


SCHEME 6.

The distribution expected according to this mechanism (2,3-DMB-2-^{13}C = 66.6%, 2,3-DMB-1-^{13}C = 33.3%) corresponds to that actually obtained.

TABLE 3

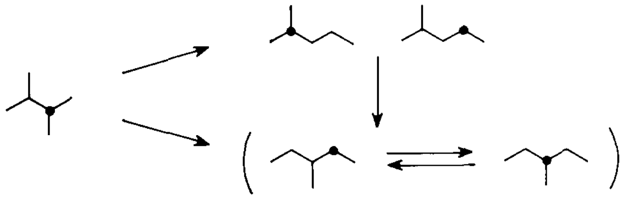
Isomerization of 2,3-Dimethylbutane: Distribution of the Monolabeled Species

Run number	Starting hydrocarbon	2,3-Dimethylbutanes			2-Methylpentanes				3-Methylpentanes			
		%[a]			%[a]				%[a]			
13		98.65	0.5	99.5	0.75	44.9	27.6	27.5	0.6	20.3	66.6	13
14		97.9	0.7	99.3	1.1	43.1	28.5	28.5	1	20.5	66.7	12.8
15		94.84	98.7	1.3	5.1	5.1	51	43.9	2.51	2.8	66.7	30.5
16		89.95	98.2	1.8	5.05	9.7	55.7	34.6	5	8.7	66.6	24.7
Scrambled distribution[b]						33.3	33.3	33.3		16.6	66.6	16.6

[a] Percentages among the monolabeled isomers.

[b] Equal distribution of the label on all six positions.

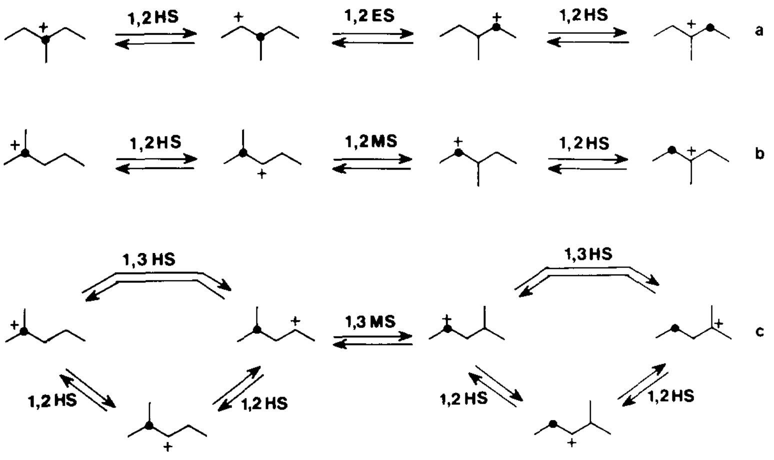
Interpretation of the labeling of 3-MP is not as straightforward since the original distribution of the species formed directly from 2,3-DMB or by isomerization of 2-MP is readily modified through the very fast 1,2-ethyl shift (Scheme 7). This is apparent from the distributions obtained in runs 15 and 16 which show that, initially, positions 2 and 3 in the 3-MP are equilibrated.



SCHEME 7.

Elementary Steps of the Rearrangements of the Hexyl Cations

Nonbranching rearrangements. The nonbranching rearrangements of the tertiary methylpentenium cations can be visualized to proceed simply by a succession of hydride shifts (HS) followed by alkyl shifts interconverting secondary cations (Scheme 8):



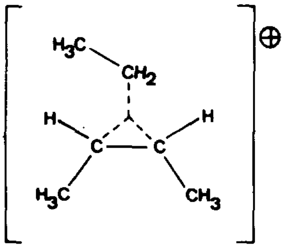
SCHEME 8.

Comparison of sequences a and b in Scheme 8 shows that the same hydride shifts (one secondary–tertiary and one tertiary–secondary hydride shift) are involved in the 1,2-ethyl shift and the 1,2-methyl shift. Since these reactions occur with different rates we must conclude that the rate-determining step of the rearrangement is the alkyl migration. For the 1,3-methyl shift (Scheme 8c) two additional secondary–secondary hydride shifts or the occurrence of direct 1,3-HS are required. If one assumes that these latter shifts are faster or as fast as a secondary–tertiary hydride shift, which is reasonable, the same conclusion, namely, that the slow step is the alkyl shift, may be drawn for the 1,3-methyl shift.

The differences observed between the

rates of the three nonbranching rearrangements are therefore due to differences in free energy between the tertiary methylpentenium cations and the transition states of the secondary–secondary alkyl shifts. The transition state for a direct 1,2- or 1,3-alkyl shift is commonly regarded as an alkyl bridged cation where the migrating group is bound to two carbon atoms by a two-electron–three-center bond. The three relevant rearrangements are tentatively represented in Fig. 2 by using Olah's notation (*7*). In the case of the 2-methylpentane, $R_1 = CH_3$ and $R_2 = H$ and Figs. 2a and c represent the 1,2-methyl shift and the 1,3-methyl shift respectively. For the 3-methylpentane, $R_1 = H$ and $R_2 = CH_3$ and Fig. 2b represents the 1,2-ethyl shift.

Our results would thus indicate that the alkyl bridged cations I to III stand in the following sequence of stabilities I > II > III.



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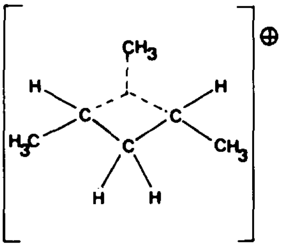

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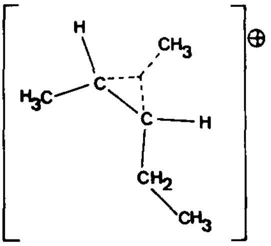
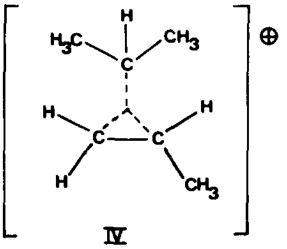


III

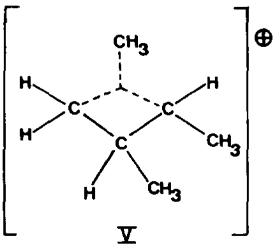
Considering the structural differences between these three species it is worthy to note that (i) the fastest migrations (1,2-ethyl shift and 1,3-methyl shift) involve the more symmetrical transition states and (ii) attachment of a methyl group to the migrating carbon atom increases the rate of an alkyl shift.

Branching rearrangements and carbon interchange. There is evidence for at least two types of branching rearrangement. The first one is that interconverting 2-methylpentane and 2,3-dimethylbutane, while the second involves a direct transformation between 3-methylpentane and 2,3-dimethylbutane. (The occurrence of this quite uncommon rearrangement has been reported once (*8*) in the reactions of hexanes over platinum deposited on a silica/alumina support but no mechanism was proposed to rationalize it.)

In a formal way the first reaction is the result of a 1,2-isopropyl shift, possibly represented by Fig. 2b with $R_1 = CH_3$ and $R_2 = H_1$, and the second corresponds to a 1,3-methyl shift as in Fig. 2c with $R_1 = H$ and $R_2 = CH_3$. The transition states of such alkyl shifts could then be pictured by cations IV and V. These are indeed very similar to cations I–III and should have comparable stabilities.



IV



V

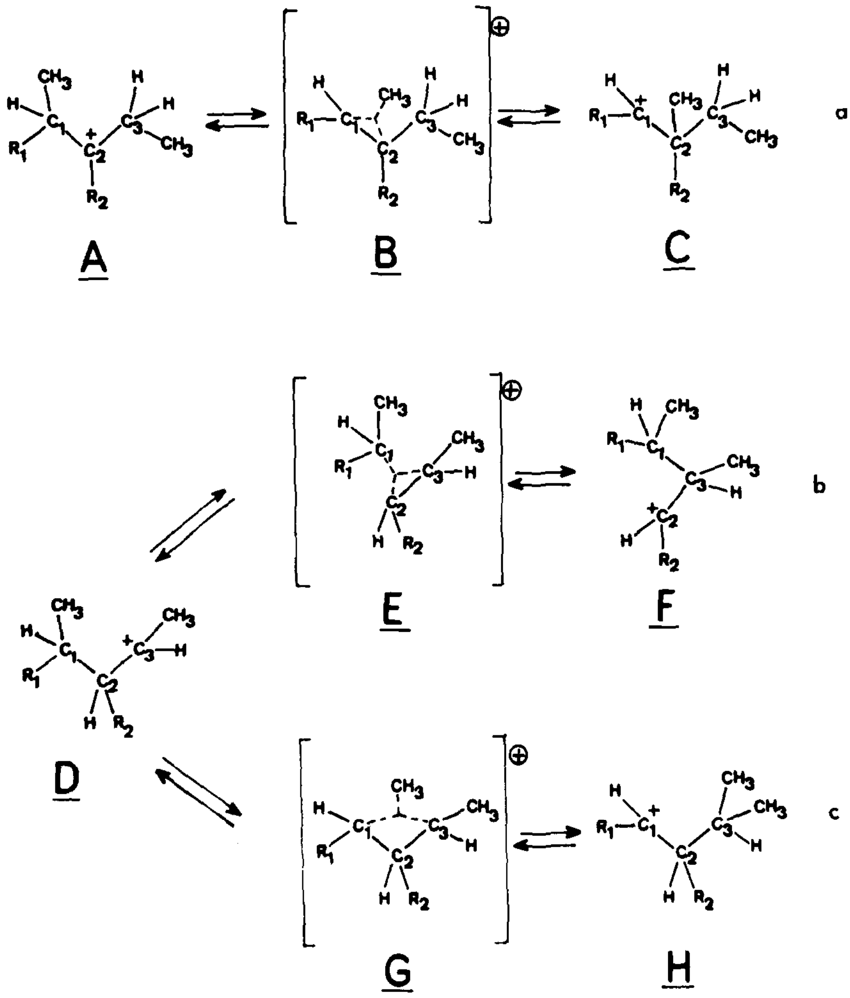


FIG. 2. Nonbranching rearrangements (see text): (a) 1,2-methyl shift, (b) 1,2-ethyl shift, and (c) 1,3-methyl shift.

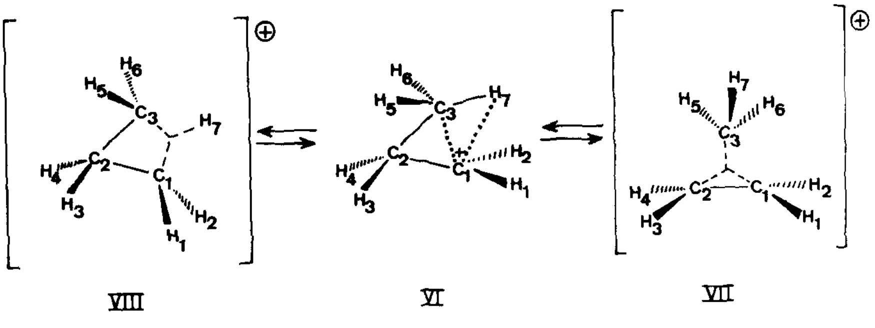


FIG. 3. Postulated representations for a distorted corner-protonated cyclopropane (VI), the transition state of the 1,2-methyl shift (VII), and the transition state of the 1,3-hydride shift(VIII) (10).

However, owing to the relatively small differences observed between the rates of the nonbranching and branching rearrangements (*1*), simple direct alkyl shifts which would transform methylpentanes into 2,3-dimethylbutanes are unlikely since both reactions would require the transformation of secondary carbonium ions into primary ones. A reaction route via protonated cyclopropane equilibration (*9*) has thus to be preferred.

Experimental data dealing with reactions requiring the intermediacy of protonated cyclopropanes have generally been interpreted in terms of direct interconversions between edge-protonated alkylcyclopropanes and alkyl-bridged cations or corner-protonated alkylcyclopropanes, these two latter species not being distinguished. According to Olah (*7*), these interconversions cannot be achieved without going through some form of primary cation.

The ab initio molecular orbital calculations with geometry optimization on the $C_3H_7^{\oplus}$ cations of Radom *et al.* (*10*) show that, though the energy differences between the various structures are relatively small, a definite potential minimum is found for the methyl eclipsed form of the 1-propyl cation (VI in Fig. 3) in which a weak but significant bonding exists between C_1 and C_3 and also C_1 and H_7 (represented by dotted lines in the figure). This cation, which can be regarded as a distorted corner-protonated cyclopropane, may rearrange by 1,2-methyl shift or 1,3-hydride shift through alkyl-bridged (VII) or edge-protonated cyclopropane (VIII) transition states and could be therefore considered as the intermediate in the reactions involving equilibration of protonated cyclopropanes.

These considerations led us to adopt the formalism in Fig. 4a for the representation of the branching rearrangement between 2-methylpentane and 2,3-dimethylbutane. A very similar scheme could account for the direct interconversion between 3-methylpentane and 2,3-dimethylbutane (Fig. 4b) provided that reaction intermediates such as *D'* and *G'* where a methyl group interacts with the positively charged carbon atom are formed. From a theoretical point of view there is no opposition in writing structures analogous to VI where H_7 is replaced by a methyl. In fact, the resulting structures (which could be defined as distorted corner-methylated cyclopropanes by analogy with the terminology of Radom *et al.* (*10*)) should be even more stable than a distorted corner-protonated cyclopropane since the partial bonding between a methyl group and the carbon atom bearing the positive charge can be expected to be stronger than that between H_7 and C_1 in VI.

As can be seen in Fig. 4b, rearrangement of these intermediates via edge-protonated alkylcyclopropanes and alkyl bridged transition states interconverts 3-methylpentane and 2,3-dimethylbutane.

The last rearrangement to be considered is the so-called carbon interchange reaction. Such a process is essentially the same as the carbon scrambling in the propyl (*11*) and sec-butyl (*12*) cations and is best described by a route comparable to that represented Fig. 4, that is, involving equilibration of protonated cyclopropane structures (Fig. 5).

CONCLUSIONS

The skeletal rearrangements of methylpentanes and 2,3-dimethylbutanes have been studied over H-mordenite at 170°C by using the ^{13}C tracer technique. Cracked products include isobutane, isopentane, and isohexanes. The ^{13}C distribution of these products corresponds to the statistical association of ^{13}C and ^{12}C carbon atoms. Their formation is explained by a polymerization–depolymerization process. The initiation step of the cracking is a β-fission of the 2-methylpentenium-4 cation yielding propene and propenium ion.

Intramolecular isomerization of the tertiary hexyl cations involves, besides classical rearrangements (1,2-methyl shift and in-

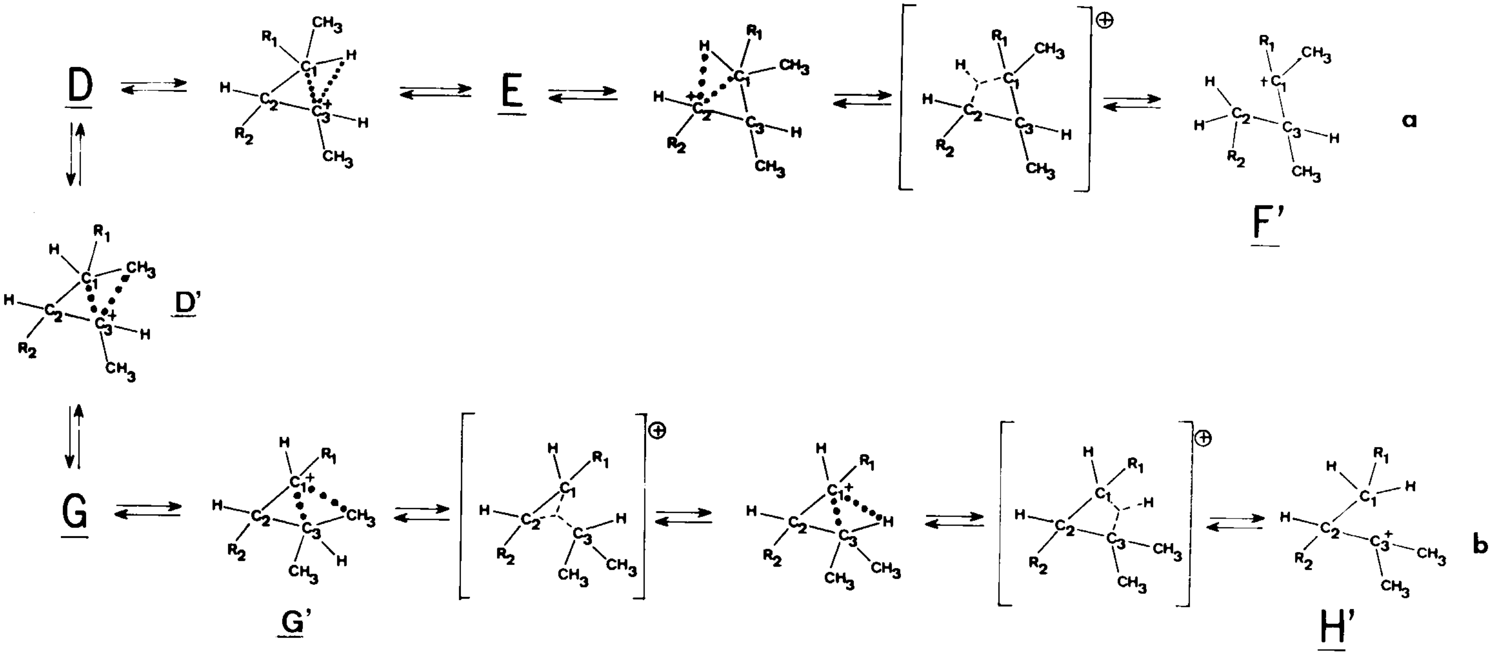


FIG. 4. Branching rearrangements. (a) Interconversion between 2-methylpentane and 2,3-dimethylbutane (R_1 = CH_3 and R_2 = H). (b) Interconversion between 3-methylpentane and 2,3-dimethylbutane (R_1 = H and R_2 = CH_3).

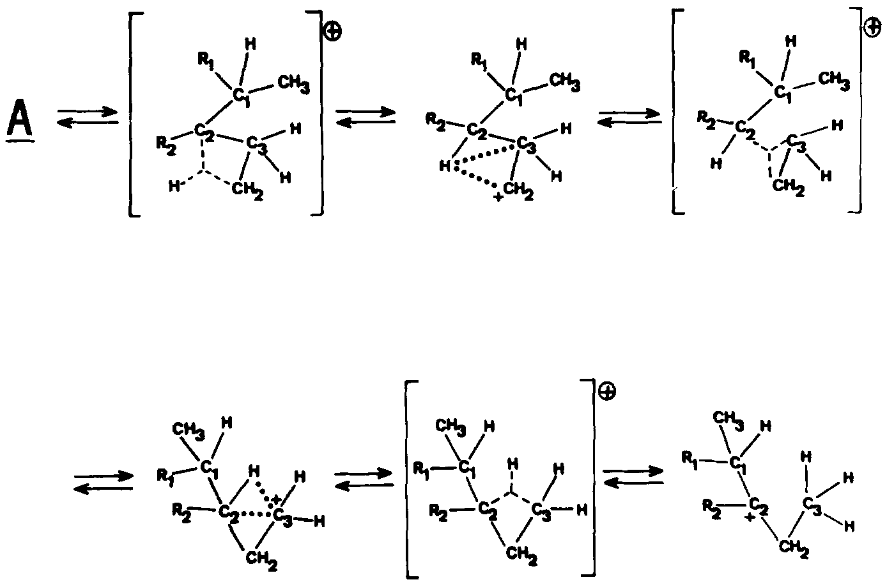


FIG. 5. Internal–external carbon interchange. Interchange between carbon C_3 and a methyl group in the 2-methylpentane ($R_1 = CH_3$; $R_2 = H$) or the 3-methylpentane ($R_1 = H$; $R_2 = CH_3$).

terconversion between 2-MP and 2,3-DMB), the occurrence of 1,2-ethyl shift, 1,3-methyl shift, direct transformation between 3-MP and 2,3-DMB, and internal–external carbon interchange. These rearrangements can be divided into two types:

In the first one we find the 1,2-ES, the 1,3-MS, and the 1,2-MS which take place simply via alkyl bridged cations as transition states. The relatives rates of these direct alkyl shifts, correlated to the relative stabilities of the transition states, are in the following sequence: 1,2-ES > 1,3-MS > 1,2-MS.

The second type of rearrangement involves the two branching rearrangements (2-MP ⇄ 2,3-DMB and 3-MP ⇄ 2,3-DMB) and the carbon interchange reaction. Equilibrations between protonated alkylcyclopropane structures are required to achieve all three reactions.

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