Skeletal Rearrangement of ^{13}C Labeled Methylpentenes and Methylhexenes on Supported *p*-Toluenesulfonic Acid

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Abstract: The skeletal rearrangements of 2-methylpentenes, 3-methylpentenes, 2-methylhexenes (exclusively alkyl shifts), and the double bond migrations which occur simultaneously have been studied at 74 °C over *p*-toluenesulfonic acid supported on silica. The rates are of the same order of magnitude for both types of reactions, except for the interconversion between 2-methylpent-2-ene and 2-methylpent-1-ene which is extremely fast. The use of ^{13}C labeled hydrocarbons demonstrates the occurrence, besides the 1,2-alkyl shift, of *direct* 1,3-methyl shift and of even more intricate skeletal rearrangements. For example, 2-methylpentenes-*3*-^{13}C and 2-methylpentenes-*5*-^{13}C are formed in equal amounts from 2-methylpentenes-*1*-^{13}C. Side-protonated, corner-protonated, and 1,3-C-methonium ion are required as intermediates to account for these products. Moreover 2-methylhexenes-*2*-^{13}C yields, besides the 3-methylhexenes-*2*-^{13}C (60%) expected by 1,2-alkyl shift, 3-methylhexenes-*5*-^{13}C (20%) and 3-methylhexenes-*3*-^{13}C (20%). The formation of these "abnormal" products necessitates, besides the classical carbenium ions, the occurrence of 1,4-C-methonium ion and of side- or corner-protonated cyclopentanes. The location of the carbon-13 in each individual isomeric olefins has been determined in the isomerization of 2-methylpent-1-ene-*2*-^{13}C and 2-methylpent-2-ene-*2*-^{13}C. Appreciable amounts of 2-methylpent-2-ene-*4*-^{13}C and 4-methylpent-2-ene-*2*-^{13}C were found in the approximate ratio 20 to 1, while 2-methylpent-1-ene-*4*-^{13}C could not be detected. These results, together with the initial product distributions obtained in the isomerization of 4-methylpent-2-ene and 2-methylpentenes-*2*-^{13}C show the following sequence for the rates of the various elementary steps: desorption of a tertiary carbenium $\gg$ desorption of a secondary carbenium ion to form a trisubstituted olefin $>$ alkyl shifts $>$ tertiary–secondary hydride shift $>$ secondary–secondary hydride shift $\gg$ desorption of a secondary carbenium ion to form a disubstituted olefin. It is suggested that this latter process, or the reverse (protonation of a disubstituted olefin), or a secondary–tertiary hydride shift is the rate-determining step in the isomerization of methylpentenes on supported *p*-toluenesulfonic acid. Some of the striking differences observed between the reactions on supported PTS acid and the ones occurring in acidic solution may be explained by the particularities of the heterogeneous system: A strong bond between the organic cation and the rigid counteranion could account for the very slow desorption of the disubstituted olefins, while the 1,3-alkyl shift and other "abnormal" skeletal rearrangements could be explained by 1,3- and 1,4-hydride shifts involving a concerted participation of several adsorbed *p*-toluenesulfonic acid molecules.

Introduction

The nature of the active sites, of Bronsted or Lewis types, on a solid acid catalyst such as silica–alumina, zeolites and so on, is still a matter of controversy. It is therefore interesting to use *p*-toluenesulfonic (PTS) acid supported on silica to demonstrate the typical behavior of a pure Bronsted acid catalyst. Recently a careful study of the isomerization of butenes on supported PTS acid showed that the intramolecular hydride shift in a carbonium ion on the solid catalyst was much slower than that in the liquid phase.[1] This very important result, if it can be extended to other olefins, makes possible and attractive a study of the mechanisms of the skeletal rearrangements which occur when olefins are contacted with heterogeneous Bronsted acid catalysts.

In the present work, the isomerization of methylpentenes and methylhexenes labeled with carbon-13 in various positions has been investigated. The advantage of using a ^{13}C tracer technique is apparent from previous works in the field of metal catalysis.[2,3]

Experimental Section

Materials. Alcohols. The synthesis of selectively ^{13}C labeled methylpentanols has been described.[2a] The same procedure, i.e., the reaction of ketone, aldehyde, or ester with alkylmagnesium halide, has been used to prepare the various ^{13}C labeled 2-methyl- and 3-methylhexanols with a reasonable yield (65–70%) (Table I).[4] The isotopic purity of the starting materials, methyl (^{13}C) iodide, ethyl-*1*-^{13}C and -*2*-^{13}C iodide, acetone-*2*-^{13}C, and ethyl acetate-*1*-^{13}C, obtained from Merck Sharp & Dohme (Canada), was in some cases around 60% and in some cases around 90%.

Hydrocarbons. All the possible ^{13}C labeled 3-methylhexanes and the 2-methylhexane-*2*-^{13}C used for the catalytic experiments and the mass spectrometrical calibrations were prepared as already described[2a,3] from the appropriate labeled alcohols by catalytic dehydration and hydrogenation on highly selective catalysts in a pulse flow system. The labeled olefins were obtained similarly by catalytic dehydration of the labeled alcohols and gas chromatographic separation of the positional isomers. The unlabeled hydrocarbons were Fluka puriss grade and used without further purification.

Catalyst. *p*-Toluenesulfonic acid supported on silica was prepared according to Sakurai et al:[1] 3 g of silica were impregnated with a solution of 3 g of monohydrated paratoluene sulfonic acid (Fluka puriss grade) in 80 ml of anhydrous ether. The ether was then evaporated and the catalyst outgassed overnight under 10^{-2} Torr at 40 °C. The silica used was pure Davisson grade (surface area: 700 m^2/g; porous volume: 40 ml/g; particle size: 60–200 mesh).

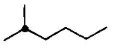
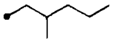
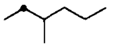
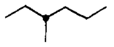
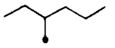
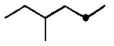
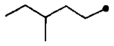
Apparatus and Procedure. The catalytic reactions were carried out in an all-glass, grease-free flow system. A small amount of reactant (ca. 4 mg) was injected at a constant pressure (6 Torr for hexenes, 1 Torr for heptenes), in a flow of purified hydrogen (1 atm, 10 ml/min) in the reactor where the catalytic bed (500 mg), isothermal and isobaric, operated under differential conditions. The details of the apparatus as well as the device to measure the hydrocarbon flow rate and the procedure to collect samples for GLC and mass spectrometrical analysis are described in ref 3.

GLC Analysis. A 5 m × ⅛ in. column of DC-200/firebrick operating at 45 °C was used for the analysis of the various olefins and a 5 m × ¼ in. column of SE-30/firebrick for the preparative separation at 24 °C.

Mass Spectrometrical Analysis. a. Procedures. Two procedures were used to obtain the mass spectra of the various reaction products. In the first one, the various olefins were separated by gas chromatography, each molecule hydrogenated on 10% Pt-Al$_2$O$_3$ at 120 °C, and the mass spectrum of the resulting paraffin was recorded after introduction into the ionization chamber through the direct inlet system of a CH7 mass spectrometer. When using this procedure, the accuracy of the location of the labeling carbon-13 was ±0.5%. In some control experiments, hydrogenations were effected on platinum black at 50 °C in order to check that no ^{13}C scrambling due to some rearrangement on the support was occurring during the hydrogenation on Pt-Al$_2$O$_3$.

In most experiments, the mixture of olefins was hydrogenated, and the resulting paraffins were analyzed by using a mass spectrometer–

Table I. Synthesis of Labeled C_7 Alcohols

Carbon skeleton	RC(=O)R'	R"MgX	RR'R"COH
	Acetone-*2*-^{13}C	BrMg-*n*-Bu	2-Methyl-2-hexanol-*2*-^{13}C
	2-Methylpentanal	$IMg^{13}CH_3$	3-Methyl-2-hexanol-*1*-^{13}C
	2-Methyl-2-pentanone	$IMg^{13}CH_2CH_3$	3-Methyl-3-hexanol-*2*-^{13}C
	Ethyl acetate-*1*-^{13}C	BrMgEt BrMgPr	3-Methyl-3-hexanol-*3*-^{13}C[a]
	3-Hexanone	$IMg^{13}CH_3$	3-Methyl(^{13}C)-3-hexanol
	2-Methylbutanal	$IMg^{13}CH_2CH_3$	4-Methyl-3-hexanol-*2*-^{13}C
	3-Methylbutanal	$IMgCH_2{}^{13}CH_3$	4-Methyl-3-hexanol-*1*-^{13}C

[a] Together with 3-methyl-3-pentanol-*3*-^{13}C and 4-methyl-4-heptanol-*4*-^{13}C. The separation of the resulting labeled saturated hydrocarbons obtained by dehydration and hydrogenation of the mixture of alcohols is easily effected by gas chromatography.

Table II. Values of a_n for the Various Labeled 3-Methylhexanes

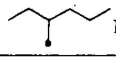
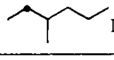
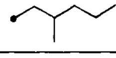
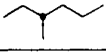
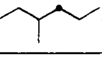
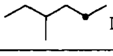
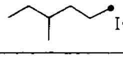
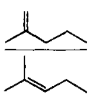
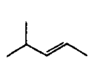
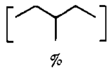
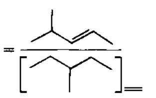
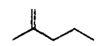
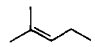
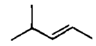
	 I-X	 I-Y	 I-Z	 I-T	 I-U	 I-V	 I-W
a_6	0.096	0.997	0.946	1.000	1.000	1.000	0.96
a_5	0.9595	0.1105	0.1105	0.933	0.95	0.991	0.95
a_4	0.9005	0.921	0.947	0.929	0.100	0.105	0.100

Table III. Isomerization of 2-Methylpentenes Product Distributions

Run	Reaction hydrocarbon		 %	 %	$\rho =$ 
1		0.18	10	6.4	1.56
2		0.16	4.3	1.8	2.38
3		0.17	4.1	1.2	3.4
4		0.17	3.6	1.6	2.25
5		0.18	3.8	1.1	3.45
6		0.20	4.3	2	2.15
7		0.17	11.8	9	1.31
8		0.20	75.7	4.2	

gas chromatograph coupling device. The experimental conditions of the chromatography (5 m × ⅛ in. 5% DC-200/firebrick; helium flow rate: 8 ml/min; entrance pressure: 2 atm, −10 °C) and the scanning speed (1.2 s/decade) used to record the mass spectra were chosen so that (a) the accuracy of the measurement on the mass spectra was only limited by the determination of the height of the peaks; (b) the change of the total ion current was smaller than 0.5% for a group of ten masses, even on the steepest part of the chromatograph elution peak.[3b] In spite of these precautions, the absolute uncertainty in determining the location of the labeling atom was higher than with the preceding procedure (1 to 2%), presumably on account of a change in the source pressure and temperature when the hydrocarbons were eluted from the chromatography column.

b. Calculations. From the recorded mass spectra, after the usual corrections for background, naturally occuring isotopes, and fragmentation, the percentage of each isotopic species in a mixture of hydrocarbons labeled in the various positions was obtained: (a) by calculating the mole fractions a_n of the ions $C_nH_{2n+1}{}^+$ which have retained the carbon-13 during their formation from an isotopically pure labeled hydrocarbon and (b) comparing these values (a_n) with the ones obtained for the various isotopic species (a_{ni}):

$$\Sigma c_i a_{ni} = a_n$$

$$\Sigma c_i = 1$$

c_i and a_{ni} are the concentrations and the mole fractions of the heavy $C_nH_{2n+1}{}^+$ ions in the *i*th isotopic species, respectively.

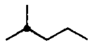
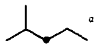
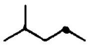
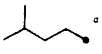
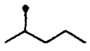
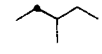
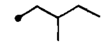
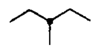
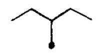
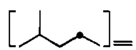
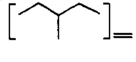
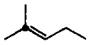
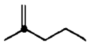
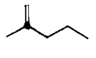
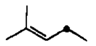
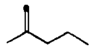
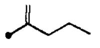
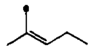
The location of the carbon-13 in the labeled 2-methyl- and 3-methylpentanes has already been discussed.[2,3] In a mixture of labeled 3-methylhexanes, the location of the carbon-13 is determined by using the $C_6H_{13}{}^+$, $C_5H_{11}{}^+$, and $C_4H_9{}^+$ ions (a_6, a_5, a_4, respectively). The a_n values of the reference hydrocarbons are reported in Table II.[4] When a value of 1 is found for a_6, species I-X, I-Z, and I-W are absent from the reaction mixture, and a_5, a_4 allow one to calculate accurately the percentage of I-Y, I-T, and of the sum I-U + I-V.

Results

Isomerization of 2-Methylpentenes. The isomerization (double bond migration and skeletal rearrangement) of 2-methylpent-1-ene (2MP-1), 2-methylpent-2-ene (2MP-2), and 4-methylpent-2-ene (4MP-2) in the presence of supported *p*-toluenesulfonic acid has been investigated at 74 °C. The distributions of the products, which include 2-methyl- and 3-methylpentenes exclusively, are given in Table III.

The equilibrium between 2-methylpent-1-ene and 2-methylpent-2-ene and between 3-methylpent-2-ene (3MP-2) and 2-ethylbut-1-ene (2EB-1) are achieved in any experiment whatever the reacting olefin might be. Values of 0.18 ± 0.02 and 25 ± 2 were found for the equilibrium ratios 2MP-1/2MP-2 and 3MP-2/2EB-1, respectively. On the other hand, the amounts of 4-methylpent-2-ene and 3-methylpentenes obtained from 2MP-1 and 2MP-2 are of the same order of magnitude. The ratio ρ = 4MP-2/3MP-2 does not depend upon the nature of the reacting olefin but increases when the conversion is decreased. The extrapolation of ρ at zero conversion gives a value of 5 ± 1 (Figure 1).

Table IV. Isomerization of Labeled 2-Methylpentenes Distribution of the Various Species

Run	Reacting hydrocarbon	2-Methylpentenes				3-Methylpentenes			
		 or  [a]	 or  [a]		Total %	 or  [a]			ρ' =  / 
9	 (75%)	92.5	7.5	0	2.5	89	11	0	3
10	+	96	4	0	3	88	12	0	1.3
11	 (25%)	94.5	5.5	0	2	88	12	0	2.7
3		96.5	3.5	0	1.2	85	15	0	3
5		98	2	0	1.1	89	11	0	1.9
12		6.7	93.3	0	11	88	12	0	0.6
13	 or  (25%)  (75%)	3.5 ± 0.8	4 ± 0.8	92.5	6	46.5	12	41.5	1.2

[a] Most probably in run 13.

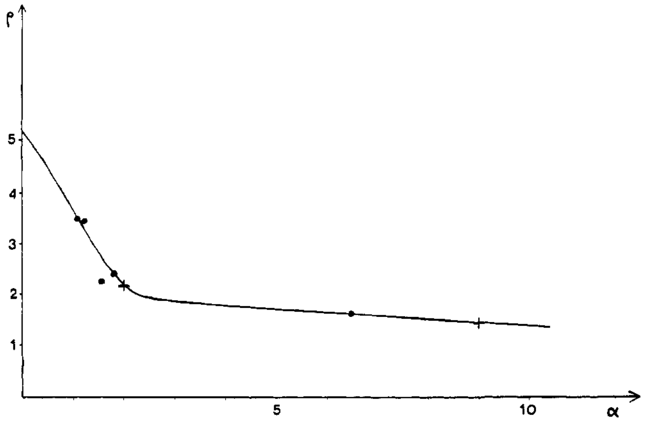
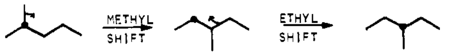


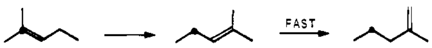
Figure 1. Ratio ρ = 4-methylpent-2-ene over 3-methylpentenes vs. α, percentage of 3-methylpentenes. Reacting hydrocarbon: ●, 2-methylpent-1-ene; ×, 2-methylpent-2-ene.

Additional experiments were done with hydrocarbons labeled with carbon-13: most of them were performed either with 2-methylpent-1-ene-*2*-^{13}C or with a mixture 3/1 of 2-methylpent-2-ene and 2-methylpent-1-ene-*2*-^{13}C. The distributions of various labeled hydrocarbons obtained after reaction and hydrogenation are given in Table IV. The major reaction product, 2-methylpentene-*4*-^{13}C, results from a 1,3-methyl shift. The "normal" product, 3-methylpentene-*2*-^{13}C, which results from a 1,2-methyl shift, is most generally formed in smaller amount. However, the ratio ρ' 2-methylpentene-*4*-^{13}C over 3-methylpentenes varies between large limits: 1.3 to 3, and in some experiments is smaller than 1. Besides the two major reaction products 2-methylpentenes-*4*-^{13}C and 3-methylpentenes-*2*-^{13}C, an "abnormal" compound 3-methylpentene-*3*-^{13}C is also obtained, and the percentage of this compound among the total 3-methylpentenes, 13 ± 2%, is remarkably constant. The location of the labeling atom in this "abnormal" compound may be formally explained by the succession of a methyl and an ethyl shift.



In order to check the 1,3-methyl shift, the isomerization of 2-methylpent-2-ene-*4*-^{13}C and of a mixture 3/1 of 2-methylpent-1-ene and 2-methylpent-2-ene-*1*-^{13}C were effected under the same conditions. 2MP-*4*-^{13}C yields 2MP-*2*-^{13}C besides 3-methylpentenes-*2*-^{13}C and -*3*-^{13}C. Unexpectedly, the 2-methylpentenes labeled at carbon 1 yields in approximately equal amounts 2-methylpentene-*5*-^{13}C and 2-methylpentene-*3*-^{13}C (or -*2*-^{13}C since both hydrocarbons are not distinguishable by mass spectrometry). Among the 3-methylpentenes, besides 3-methylpentene-*1*-^{13}C, methyl(^{13}C)-3-pentenes are also obtained in appreciable amount.

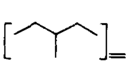
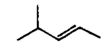
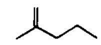
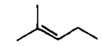
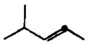
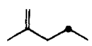
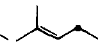
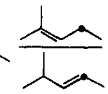
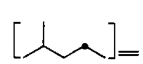
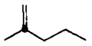
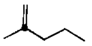
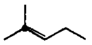
In some experiments performed with 2-methylpent-1-ene or pent-2-ene-*2*-^{13}C, the various olefins were separated by gas chromatography, and the location of the carbon-13 was determined in each molecule by mass spectrometry. Three such experiments are reported in Table V. In the two experiments at low conversion, the 4-methylpent-2-ene and the 2-methylpent-2-ene both contained appreciable amounts of species labeled on carbon 2 and 4, respectively, i.e., resulting from a 1,3-methyl shift while the 2-methylpentene-*1*-^{13}C retains all the label on carbon 2. In run 14, where the conversion to 3-methylpentenes is much higher, an appreciable amount of 2-methylpent-1-ene-*4*-^{13}C is also formed, which results presumably from the consecutive isomerization of 2-methylpent-2-ene-*4*-^{13}C:



In the last rows of Table V the total amounts of the various labeled species are reported for each experiment. The ratio 2-methylpent-2-ene-*4*-^{13}C over 4-methylpent-2-ene-*2*-^{13}C is always very high: 10 to 20.

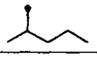
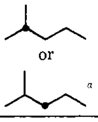
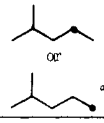
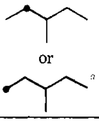
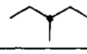
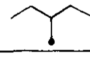
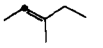
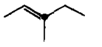
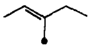
Isomerization of 3-Methylpentenes. In order to investigate further the formation of the "abnormal" 3-methylpentene species obtained from the 2-methylpent-2-enes, the isomerizations of 3-methylpent-2-ene-*2*-^{13}C, -*3*-^{13}C, and of 3-methyl(^{13}C)-pent-2-ene have been investigated under the same experimental conditions. The results are reported in Table VI. The carbon-13 is located in the 2-methylpentene products as one could have expected from a simple 1,2-methyl shift except for the small but definite amount of 2-methylpentene-*5*-^{13}C

Table V. Isomerization of Labeled 2-Methylpentenes (Location of the Carbon-13 in the Various Isomers)[a]

													
Run	Reacting hydrocarbon	%	Total %	4-^{13}C %	Total %	4-^{13}C %	Total %	4-^{13}C %	 %	 %	 %		 Total
3		1.2	4.1	4.1	14	0	80.7	4.1	0.17	0	3.3	20	3.5
5		1.1	3.8	2.8	14.4	0	80.7	2.2	0.10	0	2.0	20	2.1
14		9.0	11.8	4.4	11.3	6.7	67.7	7.3	0.50	0.75	5.0	10	6.25

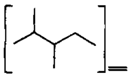
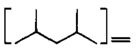
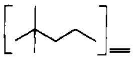
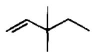
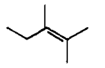
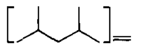
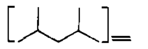
[a] The mass spectra of the saturated hydrocarbons were recorded after direct introduction of the molecules into the ionization chamber.

Table VI. Isomerization of Labeled 3-Methylpent-2-enes

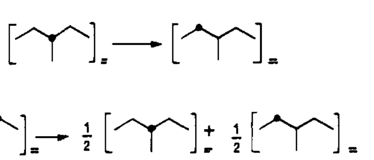
			2-Methylpentenes			3-Methylpentenes			
Run[b]	Reacting hydrocarbon	Total %							Ethyl shift / methyl shift
15		3	0	51	49	96	4	0	2.7
16		3.3	0	100	0	14	86	0	4.2
17		5	89	0	11	10	0	90	2

[a] Most probably in run 17. [b] The mass spectrometrical analysis in run 15, 16 were effected by GLC–MS coupling in run 17 by separation of the isomers and direct introduction into the ionization chamber.

Table VII. Isomerization of Dimethylpentenes

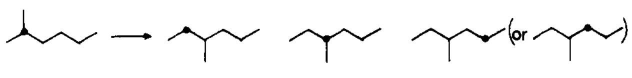
Reacting hydrocarbon					Methylhexenes	n-Heptenes
		2	4	0.2	nil	nil
	1		nil	nil	nil	nil
	3.5		<0.05	nil	nil	nil

obtained from 3-methyl(^{13}C)-pent-2-ene. Besides the 2-methylpentenes, isomeric 3-methylpentenes resulting from an ethyl shift are also formed. The ratio between the products obtained by ethyl shift and methyl shift, reported in the last row of Table VI, is always larger than 2.



Isomerization of Dimethylpentenes and 2,3-Dimethylbut-2-ene (Table VII). The isomerizations of 2,3-dimethylpent-2-ene and of a mixture of 2,4-dimethylpent-2-ene and -pent-1-ene (roughly 1/1) have been investigated on supported PTS acid at 74 °C. As in the case of 2-methylpentenes and 3-methylpentenes, neither chain lengthening nor chain shortening takes place. The only observed products result from a simple 1,2-methyl shift. It is noticeable that the 2,2-dimethylpentene which might have resulted from a 1,3-methyl shift is not formed in the isomerization of 2,4-dimethylpentenes. On the other hand, 2,3-dimethylbut-2-ene yields 3,3-dimethylbut-1-ene as the only reaction product.

Isomerization of 2-Methylhex-2-ene-*2*-^{13}*C*. Only 3-methylhexenes are obtained in this reaction. The dimethylpentenes, *n*-heptenes, and 3-ethylpentenes were looked for and could not be detected. The location of the carbon-13 in the 3-methylhexenes was determined after hydrogenation of the olefins. Three species are present: the 3-methylhexane-*2*-^{13}*C* (61%) and in equal amounts the 3-methylhexane-*3*-^{13}*C* (20%) and the 3-methylhexane-*4*-^{13}*C* or -*5*-^{13}*C* (19%) (these species



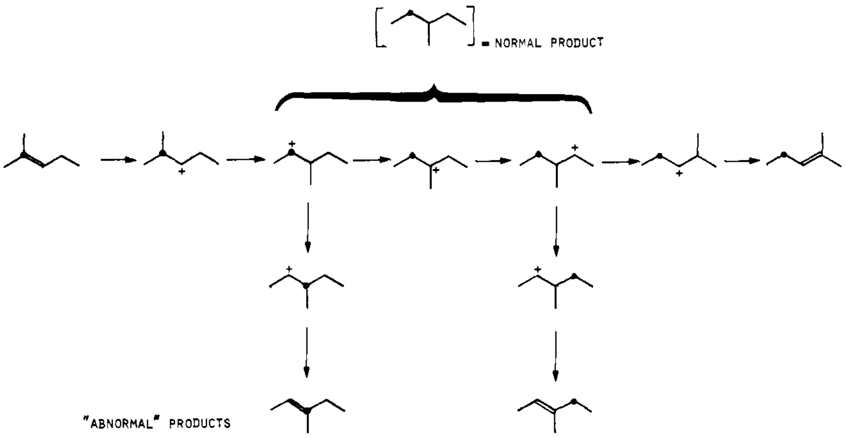
cannot be distinguished by mass spectrometry). Since $a_6 = 1$, the possibility of having any of the three hydrocarbons labeled on a terminal carbon atom is eliminated.

Discussion

Before discussing further the various reaction mechanisms, it should be emphasized again that only hydride shifts and alkyl shifts occur on supported PTS acid at 74 °C. Unlike the experiments at higher temperature on "acidic" catalysts such as silica-alumina or zeolites, neither chain lenghtening nor chain shortening takes place.

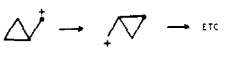
Skeletal Rearrangement of Methylpentenes. The 1,3-methyl shift demonstrated in the isomerization of 2-methylpentene-*2*-^{13}*C* and -*4*-^{13}*C* can be explained either by two consecutive 1,2-methyl shifts or by a direct process. According to the first mechanism (Scheme I), the same intermediate, i.e., a secondary 3-methylpentenium ion, should be involved in the formation of the 2-methylpentenes-*4*-^{13}*C* (2-MP-*4*-^{13}*C*) and of

Scheme I

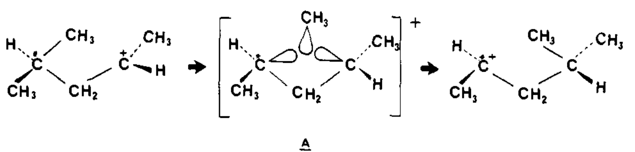


the 3-methylpentene-*3*-^{13}C (3-MP-*3*-^{13}C) which result from consecutive methyl and ethyl shifts. One should then observe the same ratio between 3-MP-*3*-^{13}C and 2-MP-*4*-^{13}C in the isomerization of 2-MP-*2*-^{13}C as between 3-MP-*3*-^{13}C and the total 2-methylpentenes in the isomerization of 3-methylpentene-*2*-^{13}C. The latter ratio, one-half of the ratio ethyl shift over methyl shift, is always larger than unity. The former one varies from one experiment to another. However, it is always smaller than 1/4 and in most experiments smaller than 1/10. Therefore the formation of 2-methylpentene-*4*-^{13}C *cannot* be accounted for by two consecutive methyl shifts, and a direct process has to be introduced, consisting of a direct 1,3-methyl shift. A further proof for the existence of this process is given by the distribution of the products obtained from 2,4-dimethylpentene. Were the 1,3-methyl shift the result of two consecutive 1,2-methyl shifts, 2,2-dimethylpentene would be formed in an appreciable amount from 2,4-dimethylpentene.

Although it was proposed many years ago by Whitmore and collaborators,[5] the direct 1,3-methyl shift has been demonstrated only in three experiments: during the dehydration of 4,4-dimethyl-3-ethyl-2-pentanol[6] and the reactions of 2-cyclopropylethylamine[7] and of 2-*α*-*H*-10-aminopinane[8] with nitrous acid. On the other hand, the unique property of the cyclopropylcarbinyl cation and in particular the scrambling of the labeling atom in tracer experiments[9] can also be represented formally by a succession of 1,3-methyl shifts. In this



case, the formation of nonclassical 1,2-C carbonium ions has been demonstrated by ^1H NMR and ^{13}C NMR spectroscopy.[10] The 1,3-methyl shift referred to,[6-8] as well as the present example, could be explained similarly by the formation, as an intermediate or an activated complex, of a 1,3-C methonium ion A.



A

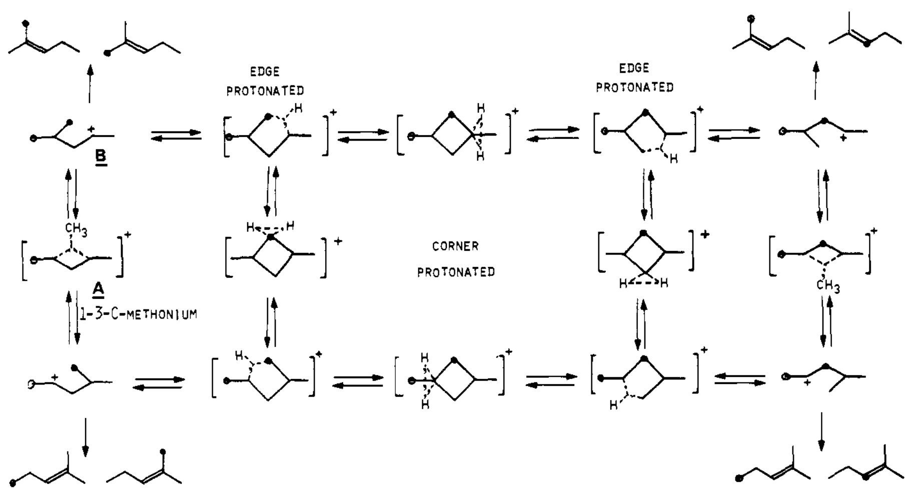
In a now classical paper,[11] Olah has proposed in the case of the norbornyl cations a series of interconversions between C-methonium ion, secondary carbenium ions, and corner- or edge-protonated cyclopropanic structures. A very similar scheme, involving 1,3-C-methonium ion, secondary carbenium ions, and corner- or edge-protonated cyclobutanes could account for the distribution of the label in the various reaction products, especially when 2-methylpent-2-ene-*1*-^{13}C is the reacting molecule. Indeed, Scheme II, and only this scheme, can account for the equal amounts of 2-methylpentene-*3*-^{13}C and 2-methylpentene-*5*-^{13}C obtained in the isomerization of 2-methylpentene-*1*-^{13}C. From a theoretical point of view, there is no opposition to the sequence outlined in Scheme II. Recently the protonation of cyclobutane has been studied theoretically by using an ab initio method:[12] essentially identical energy levels were found for edge- and corner-protonated cyclobutane. Quantum mechanical calculations are required to substantiate the occurrence of a nonclassical ion such as A, but one could expect the stability of this ion to be larger than that of a 1,2-C-methonium ion. Moreover, the 1,3-C-methonium ion may be avoided if one assumes that the two edge-protonated cyclobutane ions on the left-hand side of Scheme II and the two on the right-hand side are interconnected through corner-protonated cyclobutanes.

A question arises concerning the formation of the secondary 2-methylpentenium ion B from 2-methylpent-1-ene or -pent-2-ene. The very rapid equilibration between these two olefins strongly suggests that the initial stage of protonation yields a tertiary carbenium ion. The occurrence of B may be due then either to two successive 1,2-hydride shifts or to a direct 1,3-hydride shift. Were two consecutive 1,2-hydride shifts involved, a common intermediate would exist for both 1,3- and 1,2-methyl shifts. The ratio between 1,3- and 1,2-methyl shift varies within certain limits, which suggest that both processes occur in parallel presumably on different active sites and not via a common intermediate. For these reasons Scheme IIIb seems more likely than Scheme IIIa to describe the various reactions.

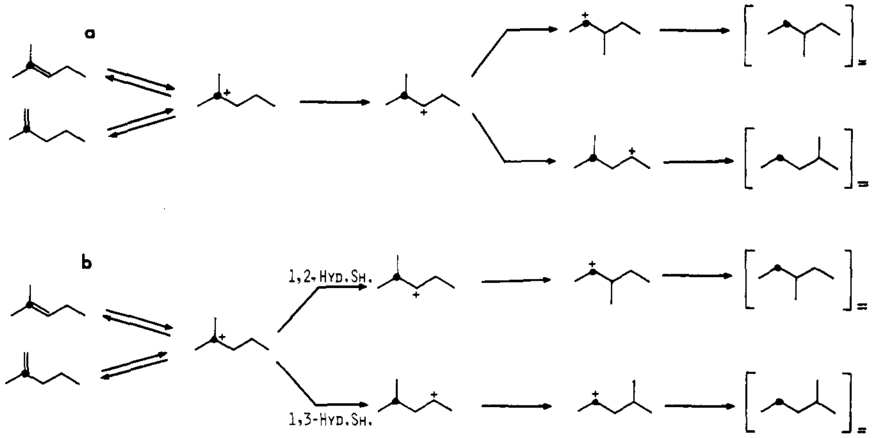
The next problem to be solved is that of the so-called ethyl shift. Such a process, according to a classical carbocation mechanism, would account for the "abnormal" 3-methylpentene species obtained from 2-methylpentenes and for the major product formed from 3-methylpentenes. However, 3,3-dimethylpentene is expected from 2,4-dimethylpentene and 3-ethylpentene from 2-methylhexene by a very similar route, and these compounds could never be detected. The only difference between Scheme IVa and Schemes IVb and IVc is the occurrence of several hydride shifts between the methyl and the ethyl shifts reaction. That could of course explain the differences observed since, as we shall see, an alkyl shift is favored vs. a hydride shift when supported PTS acid is used instead of a classical Bronsted acid in solution. An alternative explanation would involve the so-called ethyl shift as occuring via a route similar to the one described in Scheme II, i.e., involving protonated cyclobutane (Scheme V).

Methyl Shift and Hydride Shift. Since double bond migration and skeletal rearrangements occur on supported PTS acid with similar speed, it is possible to compare the rates of the various elementary steps. These elementary steps, for the isomerization of 2-methylpentenes-*2*-^{13}C, are represented in Figure 2 where b, c_2, and c_3 represent the rate constants for

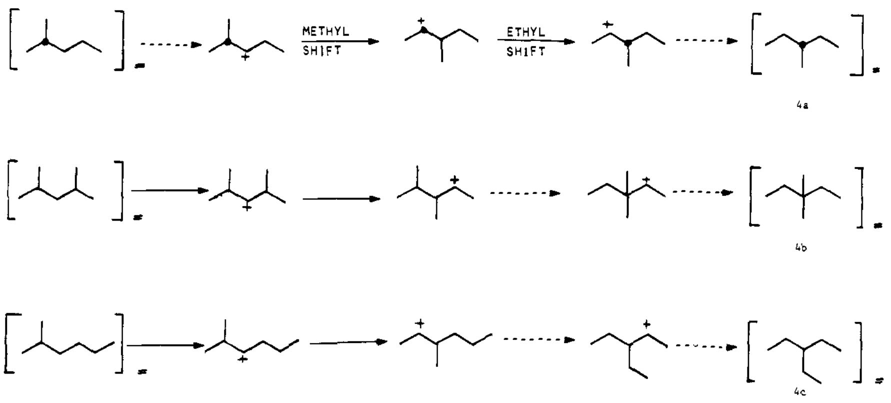
Scheme II



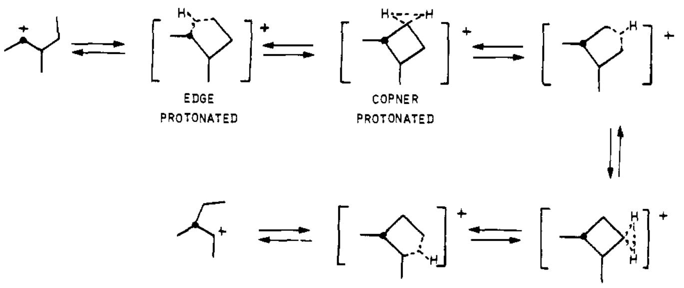
Scheme III



Scheme IV



Scheme V



deprotonation; m_{12}, m_{13}, and m_{Et} for methyl or ethyl shift; and r_{22}, r_{23}, r_{32}, and r' for hydride shifts.

The very fast equilibration of 2-methylpent-2-ene and 2-methylpent-1-ene during the isomerization of either molecule implies that for a tertiary carbenium ion, the rate constant of deprotonation (c_3) and the rate constant of the reverse reaction (c_{-3}) are much larger than the rate of 1,2- and 1,3-hydride shifts (r_{32} and r'). Moreover 2-MP-2 and 2-MP-1 are also equilibrated when obtained from 4-MP-2 which shows that c_3 and c_{-3} are larger than c_2, the rate constant of deprotonation of a secondary carbenium ion to yield a tertiary olefin.

The formation of the 2-methylpentenes-*4*-^{13}C is represented in the left lower part of Figure 2. Since 2-methylpent-1-ene-*4*-^{13}C cannot be detected, the deprotonation of S_4 is much

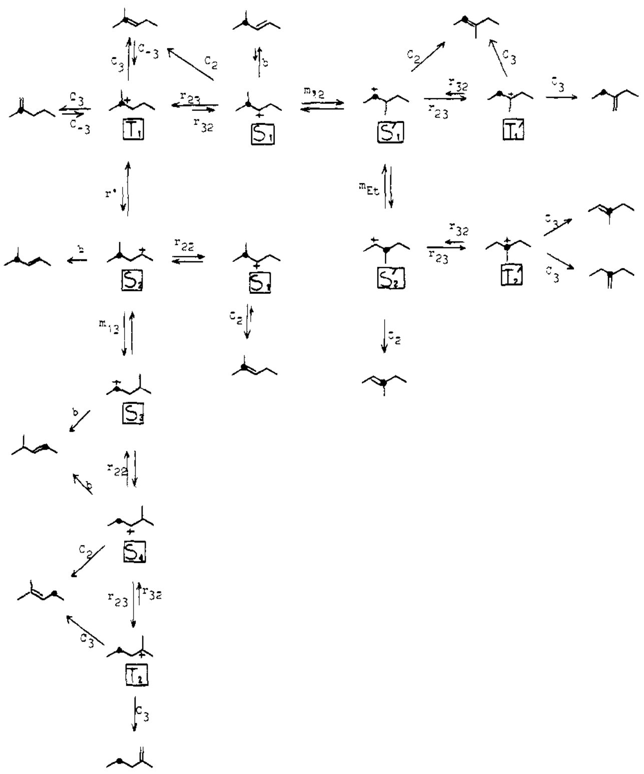


Figure 2. Reaction mechanism of the isomerization of 2-methylpentenes.

faster than its conversion into the tertiary carbonium ion T_2: $c_2 > r_{23}$. The limit of detection of an isotopic species being around 1%, an estimation of the lower limit of the ratio c_2/r_{23} may be obtained by using the data of Table III, run 3, for example:

$$c_2/r_{23} > \frac{3.3 \times 10^{-2}}{10^{-2} \times 0.14 \times 5} \simeq 5$$

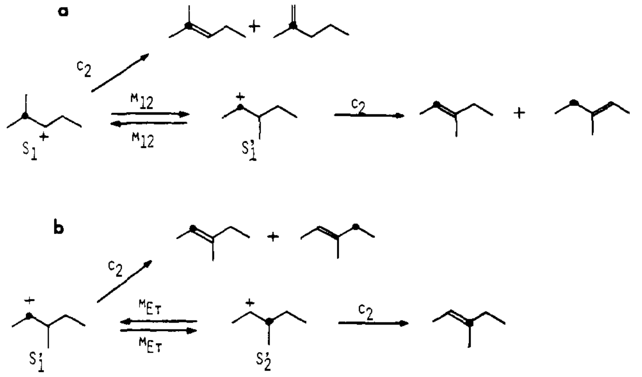
In the same experiment, the ratio 4-MP-*2-2-*^{13}C over 2-MP-*2-4-*^{13}C is equal to 20. Since the secondary carbenium ion S_4 yields not only 2-MP-*2-4-*^{13}C but can also be reverted to 4-MP-*2-2-*^{13}C or to S_3, this value (20) may be taken as a lower limit of the ratio between the rate constants of secondary-secondary hydride shift r_{22} and of deprotonation to a disubstituted olefin b: $r_{22}/b > 20$.

If one assumes then that the tertiary-secondary hydride shift is faster than the secondary-secondary hydride shift, which is reasonable, the following sequence is obtained, with a ratio c_2/b higher than 100:

$$c_3 \gg c_2 > r_{23} > r_{22} \gg b \qquad (1)$$

The competitive isomerization of 2-methylpent-2-ene-*2-*^{13}C to 3-methylpentenes-*2-*^{13}C and 3-methylpentenes-*3-*^{13}C on one hand, of 4-methylpent-2-ene-*4-*^{13}C to 2-methylpentenes-*2-*^{13}C and 3-methylpentenes on the other hand allows one to compare the rate constant of deprotonation c_2 with the rate constants of methyl shift and ethyl shift (m_{12} and m_{Et}), respectively. The branching paths are represented in Schemes VIa and VIb. Schemes VIa and VIb were simplified by neglecting the protonation reactions (reverse of c_2) and assuming that c_3, c_{-3} were much larger than c_2; Scheme VIa by supposing that the same rate constants were involved in 2 → 3 and 3 → 2 methyl shifts. Both Schemes correspond then to one single very simple kinetic model:

Scheme VI



$$\begin{tikzcd} & X_2 & \\ X_1 \arrow[ur, "k'"] \arrow[r, shift left, "k"] & X_3 \arrow[l, shift left, "k"] \arrow[r, "k'"] & X_4 \end{tikzcd}$$

in which it can easily be shown that:

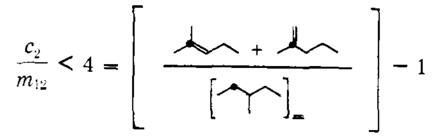
$$0 < X_4/X_2 < k/k + k' \qquad (2)$$

The two limits for X_4/X_2 corresponding to zero and infinity time.

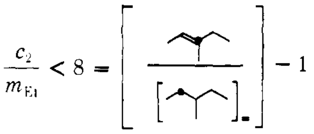
From eq 2 the following may be derived:

$$\frac{k'}{k} < \frac{X_2}{X_4} - 1 \qquad (3)$$

which in turn yields, for scheme a:



and scheme b:

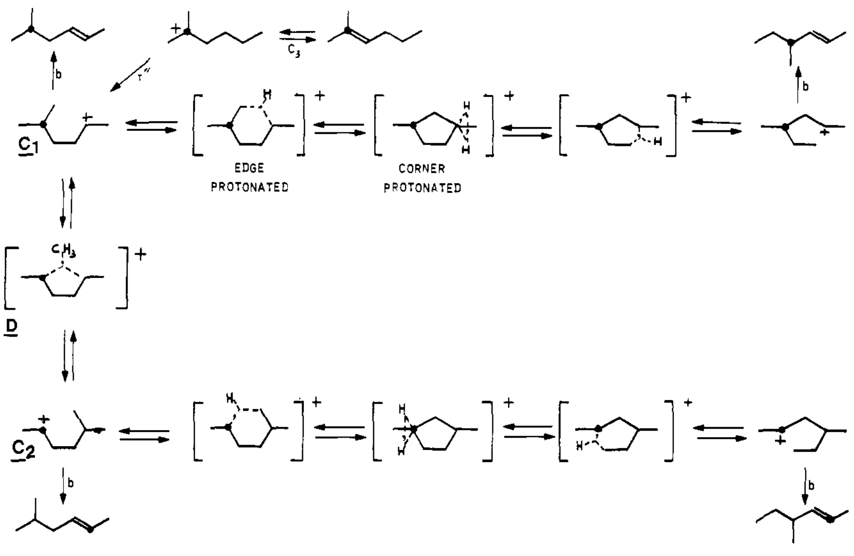


Since isomerization of labeled 3-methylpentenes has shown that an ethyl shift is slightly faster than a methyl shift, $c_2/4$ represents a lower limit for both rate constants m_{12} and m_{Et}. In sequence 1, m_{12} and m_{Et} are then inserted between c_2 and r_{23}: 1,2-methyl and -ethyl shifts are faster than *any* hydride shift.

Since the tertiary carbenium ion is much more stable than the secondary ion, the rate constant for the secondary-tertiary hydride shift r_{32} is expected to be much smaller than the rate constant for the reverse reaction r_{23}. It is therefore quite possible that r_{32} is even smaller than b, which would mean that the *rate-determining* step in the isomerization of 2-methylpent-2-ene or/and -pent-1-ene is the *1,2- or the 1,3-hydride shift* (r_{32} and r'). This view is reinforced by the fact that 4-methylpent-2-ene and 3-methylpentenes are formed in comparable amounts, while c_2 and m_{12} are much larger than b. The ratio ρ = 4-methylpent-2-ene/3-methylpentenes (larger than unity: see Table III) expresses then the ratio between the secondary-tertiary 1,3- and 1,2-hydride shifts: $\rho = r'/r_{32}$. A very similar situation arises in the isomerization of 3-methylpent-2-enes where the tertiary-secondary hydride shift is expected to also be the rate-determining step. On the contrary, in the isomerization of 4-methylpent-2-ene, the protonation of the olefin to yield a secondary carbonium ion S_1 or S_2 (reverse of step b) is most probably the rate-controlling reaction.

Among the alkyl shift occurring on supported PTS acid, the 1,3-methyl shift described in Scheme II has not been discussed yet. Scheme II involves two sets of successive parallel steps: the ones interconverting two secondary carbenium ion via a 1,3-C-methonium ion and the hydride migrations interconverting

Scheme VII



secondary carbenium ion and edge- or corner-protonated cyclobutanes. The product distribution obtained from 2-methylpent-2-ene-1-^{13}C clearly shows that all these steps are fast when compared with the deprotonation reaction (rate constant b) yielding disubstituted olefins. This does not seem unlikely since this latter reaction is very slow. On the contrary, scheme V, describing the ethyl shift as a series of interconversions between secondary carbenium ion and protonated cyclobutanes, does not appear to be valid since the 3-methylpent-2-ene formed are obtained by a very fast deprotonation reaction (rate constant c_2). Except in the case that the hydride shifts described are very fast in comparison with the classical 1,2-hydride shift, which seems very unlikely, the ethyl shift should then be considered as a true 1,2-alkyl shift.

Skeletal Rearrangement of Methyl-2-hex-2-ene-2-^{13}C. No classical 1,2-alkyl or hydride shift may account for the distribution of the labeled species. Everything happens formally as if a cyclopentane intermediate was involved in the isomerization of 2-methylhex-2-ene. We suggest the formation of a 1,4-C-methonium intermediate interconverting with protonated cyclopentane cations. Scheme VII explains the formation in equal amounts of 3-methylhexene-3-^{13}C and -5-^{13}C provided that all the hydride shifts and the interconversion between secondary carbenium ions C_1 and C_2 via a 1,4-methonium ion D are fast when compared with the desorption to disubstituted olefins (rate constant *b*).

The existence of protonated cyclopentane has as yet never been proposed. However, protonation of cyclopentane in superacid solution has been observed by Olah and Lukas,[13] resulting in ring cleavage and formation of a *tert*-amyl ion. This reaction could obviously be explained by the intervention of a protonated cyclopentane.

General Discussion

Three main results which are also three main differences between carbocation reactions on supported PTS acid and in presence of a Bronsted acid in solution[14] have been obtained in this work: (1) The methyl shifts or alkyl shifts are most generally faster than the hydride shifts. (2) The deprotonation of secondary carbenium ion to yield a disubstituted olefin is slow. (3) Besides the classical 1,2-alkyl shifts "abnormal" rearrangements such as 1,3-methyl shift and more intricate reactions take place, presumably involving nonclassical 1-*n*-C-methonium ion.

The first result does not really seem surprising. The more recent ab initio calculations on carbocations gives for the energy difference between the classical carbenium ion and the H-bridged form a value (11 kcal/mol for $C_2H_5^+$ [15]) which is not significantly different from the one between a secondary carbenium ion and a 1,2-C-methonium ion (17 kcal/mol for $C_3H_7^+$ [16]). The question is rather to understand why the hydride shift is so fast in acidic solution, as shown many times by NMR spectroscopy.[17]

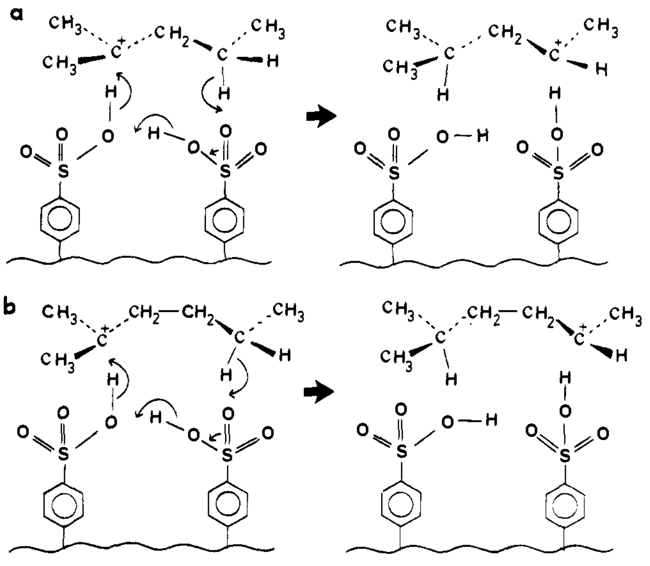


Figure 3. Concerted mechanisms of (a) 1,3-hydride shifts and (b) 1,4-hydride shifts.

The very slow rate of deprotonation of secondary carbonium ion to yield a disubstituted olefin is directly connected, we believe, with the appearance of abnormal rearrangements. As it was pointed out when discussing Scheme II and VII the 1,3-methyl shift and other reactions may be observed *only* because the alternative route, the desorption of a disubstituted olefin is not favored, presumably on account of a very strong bond between the organic cation and the supported rigid counterion. Moreover the nature of the catalyst could also favor these abnormal rearrangements inducing 1,3- or 1,4-hydride shifts by a concerted mechanism. Two such hydride shifts are tentatively represented in Figure 3a and 3b.

Similar concerted mechanisms have been proposed in order to explain the kinetics of the dehydration of an alcohol on sulfonic acid resin.[18] Although the idea of the participation of two PTS acid molecules to induce the 1,3-hydride and -methyl shift and of one PTS molecule to catalyze the 1,2-methyl shift is tempting (since it would explain by surface heterogeneity[18b] the erratic variation of the ratio between 1,3- and 1,2-methyl shifts), it should be kept in mind, however, that a nonconcerted intramolecular 1,3-hydride shift is also possible. Such a shift was demonstrated during the deamination of propylamine catalyzed by acidic solution[19-21] and led to the concept of protonated cyclopropane. Spectroscopic observation of a 1,3-hydrogen shift in the 2,4-dimethylpentyl ion was also reported by Brouwer and Van Doorn.[22] Experiments with double ^{13}C and D labeling and/or the use of deuterated catalyst are required to clarify this point.

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The Stereochemistry of Cycloadditions of Ketenes to Unsymmetrical Alkenes. Evidence for Nonparallel Transition States[1]

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Abstract: The cycloaddition of dichloroketene to 3,3-dimethylcyclopentene (**5**), 3,3-dimethylcyclohexene, 1,5,5-trimethylcyclohexa-1,3-diene, and spiro[2.4]hepta-4,5-diene, and of diphenylketene and *tert*-butylcyanoketene to **5** has been investigated. The stereochemistry of the product cyclobutanones has been determined by chemical and spectral means, including lanthanide-induced shifts in NMR. It is shown that stereoelectronic effects guide the cycloaddition to cyclohexenes, whereas steric effects predominate in analogous cyclopentene substrates. The steric results are consistent with a nonparallel transition state for addition as required by 2s + 2a or 2s + 2s + 2s mechanisms. Cycloreversion was exhibited by the adduct of **5** with diphenylketene.

Introduction

Since the discovery[2] that dichloroketene adds readily in situ to reactive olefins to yield α,α-dichlorocyclobutanones, the reaction has been the subject of a large number of synthetic and mechanistic studies.[3] The stereospecificity of the addition,[4] as well as the regioselective addition of dichloroketene to the cyclopentene double bond of dicyclopentadiene[5] and the lack of dependence on solvent polarity[4] suggest a concerted mechanism. A $\pi 2_s + \pi 2_a$ mechanism[6] is consistent with the general results for ketene–olefin cycloadditions. In such a process, the ketene plays the antarafacial role, so that, in the case of unsymmetrically substituted ketenes, the smaller substituent is preferentially oriented toward the cyclic olefin partner and predictably becomes exo in the major product.[7]

For the interaction of a symmetrically substituted ketene like dichloroketene with a simple cyclic olefin, the geometry of the transition state cannot be deduced from the products. In the case of cyclohexenes preferential axial bonding by the ketene carbonyl has been demonstrated.[3c] Although the low reactivity of dichloroketene toward norbornene[5] has been accounted for on the assumption of hindrance to the perpendicular geometry required for a $2_s + 2_a$ process, steric effects in these cycloadditions have not been evaluated, and more conclusive proof is desirable. Hence, we felt that the reaction of a ketene with an unsymmetrically disubstituted olefin might shed light on the factors influencing the cycloaddition. The more likely transition states for such an addition are pictured in Scheme I. In the least sterically hindered approach, the ketene would be expected to approach with its carbonyl end toward the substituents as shown. The overlap depicted in **2** (leading to product **4**) should be favored over **1** (leading to **3**) because rotation of the ketene in **2** moves the carbonyl group *away* from the bulkier substituent R_L. On the other hand, if the cycloaddition proceeded by way of a (forbidden) $\pi 2_s + \pi 2_s$ process, **3** would be the expected major product on steric