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Stereospecificity of Catalytic Isomerization of Olefins*

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A kinetic study of isomerization of 3,4-dimethyl-3-hexenes has been carried out over alumina and supported palladium at 250°C in a chromatographic pulse reactor. It was found that *cis–trans* isomerization of these tetrasubstituted olefins did not occur directly but necessarily proceeded through positional isomerization. This result can be interpreted by assuming that every elementary step of this reaction is stereospecific.

INTRODUCTION

Catalytic reactions are very often supposed to occur in a definite way, the adsorption on the catalyst surface implying a stereospecificity. Thus, dehydration of alcohols over alumina is known to occur by a *trans*-elimination (*1*); and catalytic hydrogenation of dienes, ethylenic and acetylenic hydrocarbons is thought to proceed through *cis*-addition of hydrogen (*2*). In fact, the results of some experiments do not perfectly agree with this hypothesis. For example, while catalytic hydrogenation of acetylenic hydrocarbons gives mainly the *cis*-ethylenic isomer, the *trans*-isomer generally exists among the products (*3*). Likewise *cis*-addition of hydrogen to the double bond of 1,2-dimethylcyclohexene and 1,2-dimethylcyclopentene would be expected to yield only the *cis*-1,2-dimethylcycloalkanes; however, both *cis* and *trans* saturated isomers are obtained (*4*, *5*).

A number of mechanisms have been proposed to account for these results. Siegel *et al.* (*6*) explain the formation of the *trans*-isomer by a mechanism involving positional isomerization of olefins followed by hydrogenation. Gault, *et al.* (*7*) suggest the concept of π-allylic intermediates undergoing *cis*- and *trans*-addition of hydrogen. It could also be supposed, according to the "roll-over" mechanism proposed by Burwell and Schrage (*8*), that the isomerization and turning over of the olefin can occur without desorption. However, none of these hypotheses can alone answer for the result obtained in the hydrogenation of 2,3-dimethyl[2,2,2]bicyclo-2-octene over platinum (*9*), the amount of *trans*-2,3-dimethyl[2,2,2]bicyclooctane in the hydrogenated mixture being larger than in the hydrogenation of 2-methylene-3-methyl-[2,2,2]bicyclooctane.

A secondary reaction for hydrogenation over metals, and dehydration of alcohols over acid catalysts, is positional isomerization which probably involves the same intermediates. In a general study of this reaction of isomerization on various catalysts (*10*), we noticed that the investigation of *cis–trans* isomerization of tetrasubstituted olefins had not yet been achieved. However, this reaction is very suitable to the testing of catalytic reactions for stereospecificity. Thus, a bi- or trisubstituted olefin can yield directly its *trans*-isomer whether all elementary reactions are stereospecific or not, but we shall see in the discussion that, if every step is stereospecific, a *cis*-tetrasubstituted olefin cannot lead initially to its *trans*-isomer. The simplest example of such a

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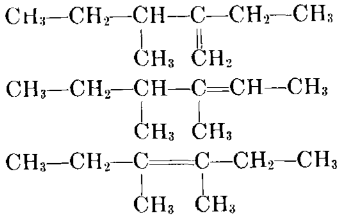
tetrasubstituted olefin is 3,4-dimethyl-3-hexene, the *cis*- and *trans*-isomers of which are separable by gas–liquid chromatography, although the meso- and *d,l*-isomers of the corresponding alkane are not resolved (*13*).

We report below the isomerization of these tetrasubstituted olefins over three catalysts where the mechanisms of reaction are probably different: an acid catalyst (alumina) over which it has generally been assumed that the surface species are carbonium ions (*11*), and two palladium catalysts. The palladium was supported on an alumina of a very small surface area. This alumina was quite inactive for isomerization. One of these palladium catalysts was used under nitrogen and the other one under hydrogen. The amount of palladium on the support and the partial pressure of hydrogen were selected so that the isomerization reaction should be fast enough and yet should not be hidden by the secondary reaction of hydrogenation.

A detailed study of *cis–trans* and positional isomerization of olefins over the same catalysts in the same conditions was previously performed (*10*). It was stated that over alumina (*12*), an associative mechanism by carbonium ions in which intermediate surface reactions was the rate-determining step could explain the experimental results. Over palladium (*10*), the results could be interpreted by a mixed mechanism involving monoadsorbed species and triadsorbed species, presumably π-allylic complexes. However, the reaction should preferentially proceed by an associative mechanism (monoadsorbed species) in the presence of hydrogen and by a dissociative mechanism (triadsorbed species) under nitrogen. Moreover, we must assume that over this catalyst, none of the elementary steps was rate controlling to account for the initial formation of 3-heptenes from 1-heptene.

Experimental Method

Olefins. 3,4-dimethyl-3-hexanol was prepared by hydrolysis of the condensation product, in a nitrogen atmosphere, of 2-butanone with magnesium *sec*-butyl bromide (yield, 22%). The dehydration of the alcohol with phosphoric acid gave a mixture of five olefins (yield, 84%).



$CH_3-CH_2-\underset{CH_3}{\underset{\vert}{CH}}-\underset{CH_2}{\underset{\Vert}{C}}-CH_2-CH_3$	3-methylene-4-methylhexane
$CH_3-CH_2-\underset{CH_3}{\underset{\vert}{CH}}-\underset{CH_3}{\underset{\vert}{C}}=CH-CH_3$	*cis*- and *trans*-3,4-dimethyl-2-hexenes
$CH_3-CH_2-\underset{CH_3}{\underset{\vert}{C}}=\underset{CH_3}{\underset{\vert}{C}}-CH_2-CH_3$	3,4-dimethyl-3-hexenes (1 and 2)

Hydrogenation over Pt/SiO$_2$ at room temperature allowed us to determine the degree of substitution of the double bond for the various isomers (*14*) and gave only one saturated hydrocarbon (*13*). The tetrasubstituted olefins were isolated by repeated distillation and preparative gas chromatography (Aerograph 700; column: Reoplex, 5 m; φ: 1 cm; 60°C; 60 cm^3/min, H$_2$) to a 99% purity. The tetrasubstitution of the double bond was confirmed by IR and NMR spectra, but their *cis* or *trans* configuration could not be assigned. Their positional isomers were not isolated except for the *trans*-3,4-dimethyl-2-hexene. This compound was identified from its IR and NMR spectra, its hydrogenation rate (*14*) and its amount in the equilibrated mixture (*10*).

Catalysts. Active alumina (Prolabo) was of 20–22 Afnor granulometry and 165 m^2/g surface area. The catalyst had been preheated in a hydrogen stream at 500°C for 6 hr.

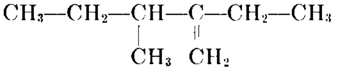
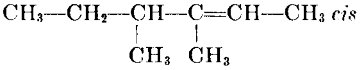
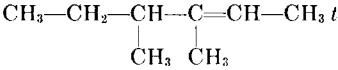
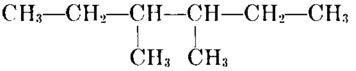
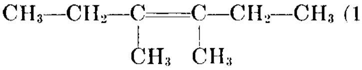
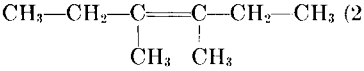
Pd/Al$_2$O$_3$: two catalysts were prepared by impregnating inactive alumina (T.F.C. Pechiney-Saint-Gobain) with a palladium chloride solution: 1 and 0.01 wt % Pd; their surface areas were very small. The reduction of the catalysts was carried out in a hydrogen stream at 400°C for 12 hr.

The Co/Al_2O_3 catalyst used to determine the composition of the equilibrated mixture of the olefins was obtained by impregnating alumina prepared according to Pines and Hagg (*15*) by hydrolysis of aluminum isopropylate. The reduction of this catalyst was carried out at 500°C for 24 hr in a hydrogen stream.

Procedure. All experiments were performed in a previously described microreactor (*14*) which was directly connected to a Perkin-Elmer F-20 chromatograph. Nitrogen was used as carrier gas during isomerization over Al_2O_3 and 1 wt % Pd/Al_2O_3 catalyst whereas a 10% hydrogen–90% nitrogen mixture was used during isomerization over 0.01 wt % Pd/Al_2O_3 catalyst. The quantity of catalyst varied according to experiments from 0.3 to 3 g and the flow of carrier gas from 150 to 900 cm^3/min.

Analysis. The reactor effluent was analyzed by the gas chromatograph which was equipped with a 50-m capillary column of squalane heated at 59°C and with a flame ionization detector.

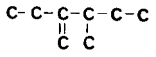
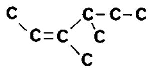
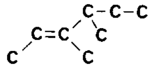
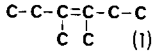
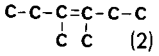
The retention times (sec) of the ethylenic and saturated hydrocarbons are:

 $\mathrm{CH_3{-}CH_2{-}\underset{CH_3}{CH}{-}\underset{CH_2}{\overset{}{C}}{-}CH_2{-}CH_3}$	854
 $\mathrm{CH_3{-}CH_2{-}\underset{CH_3}{CH}{-}\underset{CH_3}{C}{=}CH{-}CH_3}$ *cis*	889
 $\mathrm{CH_3{-}CH_2{-}\underset{CH_3}{CH}{-}\underset{CH_3}{C}{=}CH{-}CH_3}$ *trans*	922
 $\mathrm{CH_3{-}CH_2{-}\underset{CH_3}{CH}{-}\underset{CH_3}{CH}{-}CH_2{-}CH_3}$	973
 $\mathrm{CH_3{-}CH_2{-}\underset{CH_3}{C}{=}\underset{CH_3}{C}{-}CH_2{-}CH_3}$ (1)	1.016
 $\mathrm{CH_3{-}CH_2{-}\underset{CH_3}{C}{=}\underset{CH_3}{C}{-}CH_2{-}CH_3}$ (2)	1.055

The amounts of the threo- and erythro-3,4-dimethyl-1-hexenes when detected, were always very low; and they were separated from the other isomers.

RESULTS

Equilibrium. The equilibrium composition was determined at 250°C over 1 wt % Co/Al_2O_3. Various mixtures were injected, the composition of which was selected to attain the equilibrium amount of each component from both an upper and a lower value, according to the previously described method (*16*). The results are reported in Table 1.

	8.8 %
	16.6 %
	49.7 %
	12.6 %
	12.3 %

As it was not possible to assign with certainty the configuration *cis* or *trans* to the 3,4-dimethyl-3-hexenes, they were called (1) and (2) in agreement with their retention times on squalane: (1) is the more volatile of the two.

Isomerization. In the following figures, the percentages of one of the two tetrasubstituted isomers and of the sum of all the positional isomers are plotted against the percent conversion of the other.

The results of experiments over alumina at 250°C show that the direct transformation of (2) into its isomer (1) does not

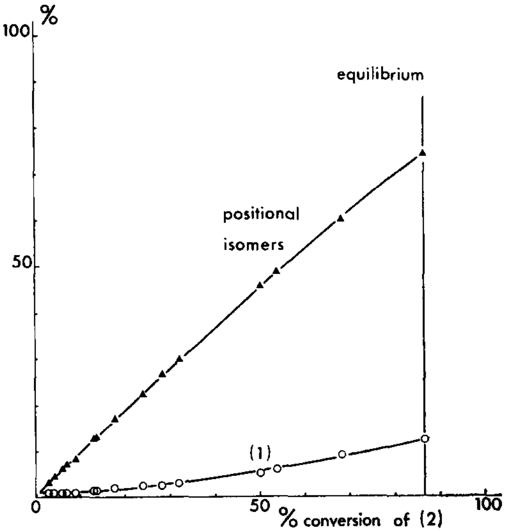


FIG. 1. Isomerization at 250°C over alumina of (2) containing 1% of (1).

take place. This can readily be seen from the curve representing the formation of (2), the slope of which is zero at the origin (Fig. 1). Symmetrically, the diagram showing the evolution of the system during the isomerization of (1) has a quite similar aspect.

The reaction conducted over 1 wt % Pd/Al_2O_3, using nitrogen as carrier gas, yielded the same results (Fig. 2). Direct *cis–trans* isomerization does not exist. The low activity of this catalyst did not allow us to obtain an important conversion.

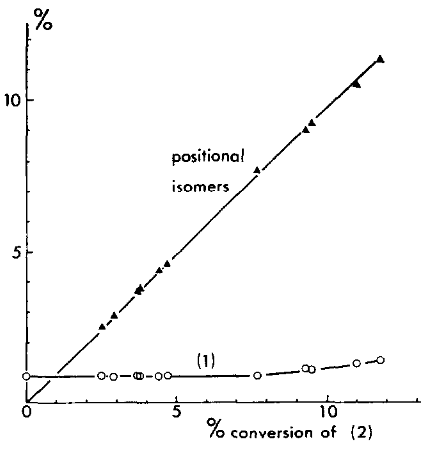


FIG. 2. Isomerization over 1 wt % Pd catalyst of (2) containing 0.9% of (1) at 250°C.

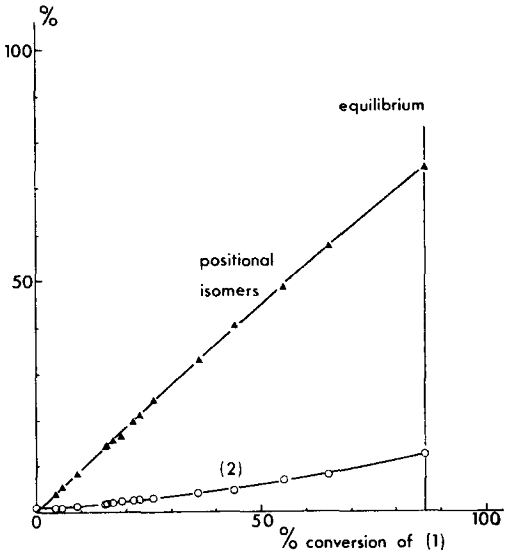


FIG. 3. Isomerization at 250°C over 0.01 wt % Pd of (1) containing 1% of (2).

With 0.01 wt % Pd/Al_2O_3 catalyst, under hydrogen–nitrogen mixture ($p_{H_2} = 0.1$ atm), the same phenomenon was observed concerning *cis–trans* isomerization: the 3,4-dimethyl-3-hexenes did not directly isomerize into each other (Fig. 3). In addition, some hydrogenation was detected but we shall not take it into account because it always remained slow with regard to the studied transformation.

DISCUSSION

We confine the present discussion about the isomerization of the 3,4-dimethyl-3-hexenes to the most classical mechanisms: associative mechanism involving monoadsorbed species (*11*, *17*); and dissociative mechanism, involving π-allylic intermediates (*18*, *19*). We shall always suppose that the olefin is first diadsorbed on the catalyst (π-diadsorbed or σ-diadsorbed) and that this step is stereospecific, the *cis*-isomer leading only to a *cis*-diadsorbed species and not to a mixture of both *cis*- and *trans*-diadsorbed species because, in this last case, direct *cis–trans* isomerization would occur, which is neither observed over alumina nor over palladium.

a. Associative mechanism (involving monoadsorbed species). The theoretical

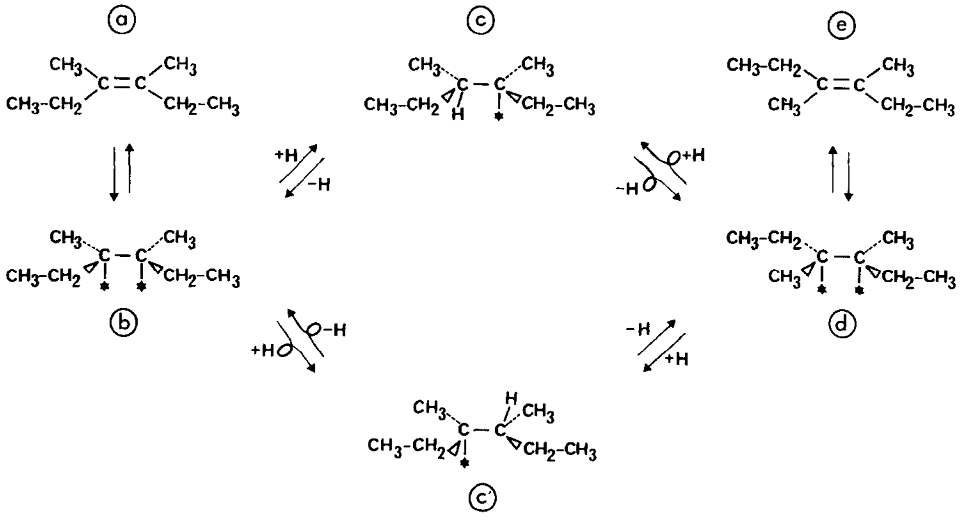


FIG. 4. Isomerization of 3,4-dimethyl-3-hexenes involving monoadsorbed intermediates: (→: *cis*-reaction; ⇢ : *trans*-reaction).

mechanism reported in Fig. 4 shows how *cis–trans* isomerization of *cis*-3,4-dimethyl-3-hexene would occur involving monoadsorbed species whatever their nature may be: carbonium ions (over alumina) or radicals (over palladium). We shall at first suppose that the sec-butyl groups of the monoadsorbed species (c) and (c′) can rotate rapidly.

Addition of hydrogen to (b) from the catalyst (*cis*-addition) yields (c) and a *trans*-abstraction of hydrogen from that intermediate (from the side opposite to the catalyst) yields (d) and then the *trans*-3,4-dimethyl-3-hexene.

Inversely, a *trans*-addition of hydrogen followed by a *cis*-abstraction would give the same diadsorbed isomer (d) via (c′). (c) and (c′) are diastereoisomers which cannot transform into each other except by inversion of the configuration at one carbon.

But if addition and abstraction of hydrogen are both *cis* or both *trans*, that is if the reactions are stereospecific, the only possible way is, for example in the case of *cis*-reactions:

$$(a) \rightleftarrows (b) \rightleftarrows (c) \rightleftarrows \text{positional isomers} \leftrightarrows (c') \leftrightarrows (d) \leftrightarrows (e),$$

where the broken arrows represent the passage from (c) and (c′) to positional isomers via the corresponding diadsorbed species.

No direct *cis–trans* isomerization between tetrasubstituted olefins was observed over alumina, where the assumed mechanism is solely associative. Yet, it has been verified that direct *cis–trans* isomerization existed for bi- and trisubstituted olefins in the same conditions (*12*). So we can conclude that over this acid catalyst every elementary step providing positional isomerization is stereospecific. This result calls for some comments: whereas in organic chemistry carbonium ions are called up to explain nonstereospecific reactions (SN_1, E_1) because of their planarity, in heterogeneous catalysis it must be assumed that the carbonium ion is always "solvated" by the solid on one of its sides; the adsorbed ion therefore is not symmetrical and might only racemize by the way of desorption followed by adsorption on the other side, transformation which is by no means to be expected here.

b. Dissociative mechanism (involving π-allylic intermediates). This mechanism which may occur over palladium only allows direct *cis–trans* isomerization of bi- and trisubstituted olefins if the intermediate surface reactions are not rate-controlling, for it is generally assumed

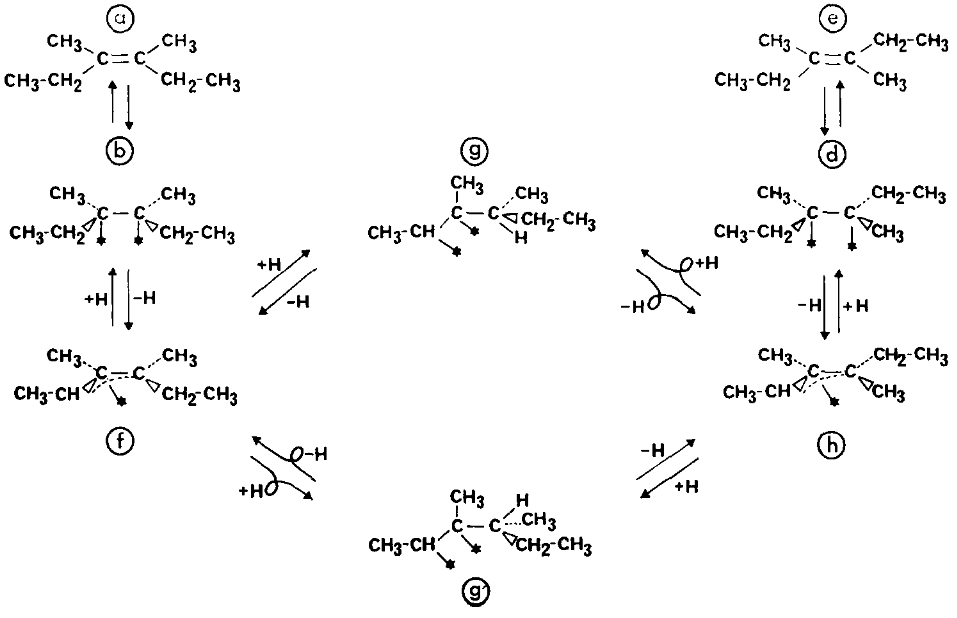


FIG. 5. Isomerization of 3,4-dimethyl-3-hexenes involving π-allylic intermediates: (→: *cis*-reaction; —○→: *trans*-reaction).

that the π-allylic species corresponding to the *cis*- and *trans*-isomers cannot be directly converted into each other (*19, 20, 21*).

The isomerization of 3,4-dimethyl-3-hexenes via π-allylic species is shown in Fig. 5. We shall again suppose that the olefin adsorption leads at first to a diadsorbed species and that free rotation is possible for the *sec*-butyl groups of the diadsorbed species (g) and (g′). We shall not detail the stereochemistry of secondary carbons. Figure 5 shows that direct *cis–trans* isomerization of tetrasubstituted olefins is only possible if, besides the condition that intermediate surface reactions are not rate-controlling, abstraction and addition of hydrogen take place in different ways. For example, abstraction of hydrogen from (b) yields (f) to which *trans*-addition of hydrogen gives (g′) then *cis*-abstraction of this hydrogen from (g′) yields (h) and the *trans*-3,4-dimethyl-3-hexene. On the other hand, *trans*-abstraction of hydrogen from (g′) would give back (f). According to the principle of microscopic reversibility, addition and abstraction of hydrogen must occur in the same way; but if these two steps can successively take place in different ways, then each of them is nonstereospecific.

The *trans*-addition of hydrogen to π-allyl complexes was proposed by Gault *et al.* (*7*) to explain the catalytic exchange with deuterium of polymethylcyclopentanes.

Thus, if the adsorption and desorption steps and the adsorbed species transformations are stereospecific, a tetrasubstituted olefin cannot lead directly to its geometric isomer except by passage through positional isomers which must desorb and then adsorb on the other side of the double bond.

No direct *cis–trans* isomerization between tetrasubstituted olefins was observed over palladium in the presence and in the absence of hydrogen, while we could again verify that with this catalyst *cis–trans* isomerization existed for bi- and trisubstituted olefins.

So, if our assumptions are correct, we can conclude that over both alumina and palladium catalysts, adsorption, desorption, and intermediate surface reactions providing isomerization are stereospecific whether the reaction proceeds through associative or dissociative mechanism.

c. Although this conclusion accounts for our results in the isomerization of the *cis*- and *trans*-3,4-dimethyl-3-hexenes, another explanation might be proposed. We have indeed supposed that free rotation was possible for *sec*-butyl groups in the monoadsorbed species (c) and (c′) of Fig. 4 and in the biadsorbed species (g) and (g′) of Fig. 5, similar assumptions being generally assumed for organic mechanisms. But these groups are bulky and rotation in the adsorbed olefin may be very slow, due to steric hindrance with the catalyst surface and this step might be rate-controlling. But we cannot avoid steric hindrance with any tetrasubstituted olefin, the skeleton chosen in this work being the simplest one. We think that by using deuterated bi- or trisubstituted olefins, we could test this hypothesis.

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