The Isomerization of Olefins
Part II. Thermal and Catalytic Isomerization of Olefins using Acids, Metals, Metal Complexes, or Boron Compounds as Catalysts

A. J. HUBERT and H. REIMLINGER

Union Carbide European Research Associates S.A., 95, rue Gatti de Gamond, Brussels 18, Belgium

Part I[1] of this review was devoted to the base-catalyzed isomerization of olefins. All other methods used to isomerize olefins are treated in Part II. As in Part I, isomerizations involving rearrangement of the carbon skeleton are not considered.

Im Teil I dieser Übersicht wurde die basen-katalysierte Isomerisierung von Olefinen besprochen. Alle anderen Methoden der Isomerisierung von Olefinen sind im Teil II abgehandelt. In beiden Teilen der Übersicht ist das Thema auf solche Isomerisierungen beschränkt, die ohne Umlagerung des Kohlenstoff-Gerüstes der Olefine ablaufen.
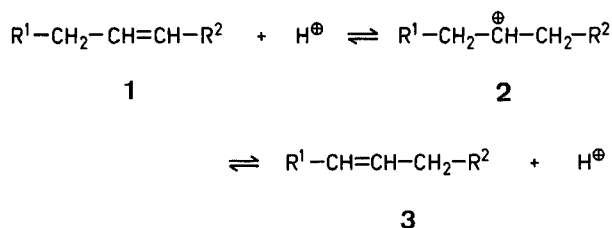
1. Isomerization of Olefinic Hydrocarbons

Acids and bases[1] are the most important catalysts for double bond isomerizations of olefinic hydrocarbons, and therefore the reactions involving these catalysts have received the predominate attention in the literature. However, during recent years, the interest in metal-, metal complex-, and boron compound-catalyzed isomerizations of olefins has increased continuously. Particularly, "contra-thermodynamic" isomerization effected by hydroboration[39], which leads to α-olefins, is of considerable preparative importance. Thermal- and radical-induced isomerizations, however, with the exception of thermal isomerizations of cycloolefins, have been studied less extensively.

1.1. Isomerization of Linear Hydrocarbons

1.1.1. Acid-catalyzed isomerizations in homogeneous solutions

Whereas the base-catalyzed isomerization of olefins[1] proceeds through carbanions, the acid-catalyzed reaction takes place via carbonium ions[2]:

$$R^1-CH_2-CH=CH-R^2 \quad + \quad H^{\oplus} \quad \rightleftharpoons \quad R^1-CH_2-\overset{\oplus}{C}H-CH_2-R^2$$

$$\mathbf{1} \qquad\qquad\qquad\qquad \mathbf{2}$$

$$\rightleftharpoons \quad R^1-CH=CH-CH_2-R^2 \quad + \quad H^{\oplus}$$

$$\mathbf{3}$$

Both isomerizations may be effected in homogeneous solutions or in the presence of a heterogeneous catalyst; both lead from a thermodynamically less-stable olefin to a more stable one.

Carbonium ions, in contrast to the carbanions encountered in base-catalyzed isomerizations, often undergo rearrangements of the carbon skeleton. The migration of a double bond, however, generally occurs more readily than skeletal rearrangements[3] (but less easily than cis-trans isomerizations), and can thus be selectively effected under appropriate conditions. When skeletal rearrangement occurs, it is often preceded by isomerization of the double bond. The order of carbonium ion stability is the reverse of that for carbanions:

tertiary > secondary > primary.

Thus, it may be assumed in general that in acid-catalyzed and thermal isomerizations, the olefin with the highest number of alkyl groups at the double bond is the most stable. For example, 2,3-dimethyl-1-butene is isomerized into 2,3-dimethyl-2-butene in the presence of sulfuric acid[5], and terminal olefins are isomerized into their internal isomers.

Non-conjugated diolefins with the double bonds in terminal positions undergo facile rearrangement to conjugated dienes[6]. This rearrangement is more difficult when one of the double bonds is buried in the chain, and is most difficult when both double bonds of the isolated diene are non-terminal.

Both Lowry-Brönsted and Lewis acids are used as catalysts. The catalytic isomerization of undecene has been studied[7] using the following acids:

H_2F_2, HBF_4, $HClO_4$, H_2SO_4, p-H_3C—C_6H_4—SO_3H, C_6H_5—SO_3H, $AlCl_3$, and BF_3.

[1] Part I: A. J. HUBERT, H. REIMLINGER, Synthesis 1969, 97.

[2] A. G. OBLAD, T. H. MILLIKEN, G. A. MILLS, Chemical Characteristics and Structure of Cracking Catalysts, Advan. Catalysis 2, 199 (1951).

[3] F. E. CONDON, Catalysis, Vol. VI, p. 43, Reinhold Publishing Corp., New York, 1958.

[4] F. A. FIDLER, The Science of Petroleum, Vol. V, Part I, (1953), p. 106, Oxford University Press.

Various solvents, acid concentrations, and temperatures were used. One of the most effective catalysts was found to be perchloric acid/acetic anhydride at 100°. This system only induced a small amount of polymerization, whereas boron trifluoride or aluminum chloride in carbon tetrachloride caused complete polymerization of the olefin after a relatively short reaction time.

The systems sulfolane/methyl bromide/tetrafluoroboric acid and sulfolane/methyl bromide/4-nitrobenzenesulfonic acid are very convenient acidic catalysts for the isomerization of octenes[8].

Isomerization of 1-undecene with 70% perchloric acid and acetic anhydride[7]: A mixture of 1-undecene (3.0 g), 70% perchloric acid (0.174 ml, 10 mol %), and acetic anhydride (to take up water) is shaken for 30 min. at 100°. The mixture is then neutralized with aqueous sodium carbonate, the organic layer separated, washed with water, dried, and distilled. G. L. C. analysis of the product indicates the presence of 4% 1-undecene, 40% 2-undecene, 28.1% 3-undecene, 18.4% 4-undecene, and 9.5% 5-undecene. The product also contains 5% polymer.

Perchloric and phosphoric acids are the most frequently used acidic catalysts for double bond isomerization[9]. Both have the advantage that they neither add to nor oxidize the olefin. It is of interest that in some cases a mixture of two acids is a more active catalyst for isomerization than either acid alone. For instance, mixtures of hydrofluoric or hydrochloric acid and alumina behave this way[9]. Addition of alumina to basic catalysts also increases the rate of basic isomerizations (see Part I[1]).

Considerable efforts of industrial research groups (see Section 3.) have been expended on the problem of isomerization of 1-butene into the 2-isomer. The reaction occurs in the presence of a variety of catalysts: copper, aluminum sulfate (at 250–300°), quartz, perchloric acid (at 21°), zinc chloride (at 100°), benzenesulfonic acid, phosphoric acid, and phosphoric acid on silica gel. In all cases, the mechanism involves hydrogen transfer between the catalysts and the olefin[10,11].

Previously proposed mechanisms for the acidic isomerization of butenes (e.g., by phosphoric acid) involved a proton addition-elimination sequence[13] or the formation of a phosphoric acid ester[12]. A "hydrogen switch" mechanism[10] was later proposed to explain facts which could not be accounted for on the basis of the previous mechanisms, i. e., the facts that ethylene does not exchange tritium[10] and that trichloroacetic acid does not isomerize 1-butene whereas sulfuric and phosphoric acids cause rapid isomerization. According to the "switch mechanism",

the bond migration is a concerted process involving activated complex 5, in which sulfuric acid (in this case) acts both as donor and acceptor for the hydrogen atoms:

4

5

6
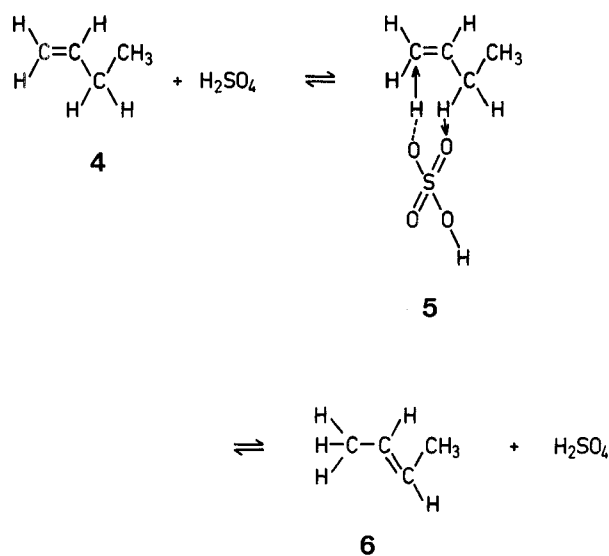
Thus, a catalyst suitable for such isomerizations should be capable[10] of simultaneously donating and accepting a hydrogen atom at centers separated by ~ 3.5 Å corresponding to the distance between the C_1- and C_3-hydrogen atoms in structure 4.

The requirement is satisfied by sulfuric acid, silicic acid, phosphoric acid, perchloric acid, $HAlBr_4$ and $HAlCl_4$. A criticism of this attractive mechanism is, however, that it does not explain the cis-trans isomerization of the olefin, which occurs at an equal or even faster rate than the double bond shift, or the skeletal rearrangements which often take place in acid-catalyzed isomerizations of olefins.

1.1.2. Isomerizations of linear olefins on heterogeneous catalysts bearing acid sites

The fact that migration of double bonds occurs on alumina is of great importance in dehydration of alcohols and in chromatography. The isomerization of double bonds on alumina is particularly fast at elevated temperatures and is therefore very frequently encountered during the dehydration of alcohols to olefins[15]. At temperatures above 300°, the tendency of terminal double bonds to migrate toward the center of the molecule is very high[16], whereas the probability of isomerization of a double bond from a highly-branched to a less-branched position is very low.

[5] A. KIRRMANN, E. SAITO, Bull. Soc. Chim. France 1945, 809.

[6] A. L. HENNE, A. TURK, J. Amer. Chem. Soc. 64, 826 (1942).

[7] F. ASINGER, B. FELL, G. COLLIN, Chem. Ber. 96, 716 (1963).

[8] M. D. CARR, J. R. P. CLARKE, M. C. WHITING, Proc. Chem. Soc. 1963, 333.

[9] F. ASINGER, B. FELL, Erdöl und Kohle 19, 258 (1966).

[10] J. TURKEVICH, R. K. SMITH, J. Chem. Phys. 16, 466 (1948).

[11] J. TURKEVICH, R. K. SMITH, Nature 157, 874 (1946).

[12] V. N. IPATIEFF, B. B. CORSON, Ind. Eng. Chem. 27, 1069 (1935).

[13] F. C. WHITMORE, J. Amer. Chem. Soc. 54, 3274 (1932).

[14] W. O. HAAG, H. PINES, J. Amer. Chem. Soc. 82, 2488 (1960).

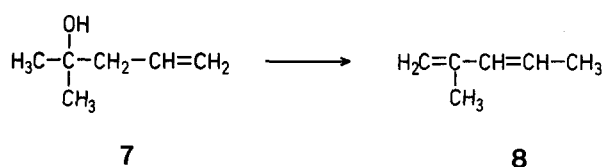[15] F. ASINGER, Chem. Ber. 75, 1247 (1942).

[16] A. A. PETROV, S. R. SERGIENKO, A. L. TSEDILINA, Y. P. EGOROV, Khim. i Tekhnol. Topliva 1956, 26; C. A. 50, 16655 (1956).

The sites of strong acidity are responsible for the double bond migration on alumina catalysts, whereas dehydration takes place on sites of lesser acidity[17].

The structure of the alumina used is very important. Thus, the ϑ-form is three times less active than the γ-form of alumina in the dehydration of butanol; and therefore the use of the former material as a dehydration catalyst involves the more severe conditions, and the higher degree of isomerization of 1-butene[18].

The dehydration of 4-hydroxy-4-methyl-1-pentene (7) on a mixture of chromium and aluminum oxides gives 2-methyl-1,3-pentadiene (8)[19]. Heating of isoamyl alcohol on alumina at 380° results in the formation of 2-methyl-2-butene plus traces of 2-methyl-1-butene[20]:

$$\underset{7}{H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2-CH=CH_2} \longrightarrow \underset{8}{H_2C=\underset{\underset{CH_3}{|}}{C}-CH=CH-CH_3}$$

The migration of double bonds on alumina or on silica gel, a phenomenon general for stationary phases containing acid sites, is sometimes troublesome during chromatography of olefins on these supports[21]. The isomerization of olefinic double bonds on alumina has been extensively reported[3,4,7,9,10,22,23]. The isomerization of 1-butene into 2-butene on alumina powder and pellets at 230° has been the subject of a mechanistic study[12]. A carbonium ion mechanism seems to explain the results better[12] than the concerted mechanism proposed for acidic isomerizations in homogeneous solution[10].

Thermodynamic data for the isomerization of 1-butene into 2-butene on a silica-alumina-magnesia catalyst have been determined[24]. The values of free energy for the isomerization of 1-butene into trans-2-butene ($\Delta F^{\circ}_{1,t} = -2.875 + 3.05 \, T$) and for the isomerization of 1-butene into cis-2-butene ($\Delta F^{\circ}_{1,c} = -2.370 + 3.00 \, T$) show that the trans isomer is more stable[24]. Other studies[25] have shown that the isomerization of 1-butene into 2-butene on a silica-alumina catalyst at 66° is stereospecific and leads to the thermodynamically unfavored cis isomer;

this isomer is favored kinetically, especially at low conversions. These results have been rationalized in terms of intermediate non-classical carbonium ions. In the isomerization of 1-butene and cis-2-butene, these ions are represented by structures 9 and 10. The stereospecificity of the reaction results from the fact that in structure 10 free rotation of the terminal C-atom to a position trans, relative to the other terminal C-atom, is impossible. Thus, only cis-2-butene is produced:

$$\underset{9}{C=\!\!=C-C\,\overset{C}{\diagup}}\qquad\qquad \underset{10}{\overset{C}{\diagdown}C=\!\!=C\,\overset{C}{\diagup}}$$

In a recent study[26] of the mechanism of butene isomerization on alumina and silica-alumina catalysts, it was shown that considerable intermolecular hydrogen exchange takes place. It was suggested that cis-trans isomerization takes place by intramolecular rearrangement; however, the degree of intramolecularity of double-bond migration is unknown. The acidity of the active sites of the silica-alumina catalyst is important in the reaction[27]; both protonic and Lewis acid sites are catalytically effective. It was found, however, that the catalysts containing sites of high acidity lead to a cis:trans product ratio of 2:1, in contrast to the case with catalysts possessing centers of lesser acidity, which give cis: trans product ratios of 1.1 to 1.3.

In the case of the widely used alumina-silica catalysts, it has also been suggested that the isomerization takes place via π-complexes at the acidic centers of the catalyst[28].

Diolefins are isomerized on alumina into conjugated olefins[29]; e.g., 1,5-hexadiene (11) forms 2,4-hexadiene (12) at 300°:

$$H_2C=CH-CH_2-CH_2-CH=CH_2 \quad\xrightarrow{\quad Al_2O_3 \,/\, 300° \quad}$$

11

$$H_3C-CH=CH-CH=CH-CH_3$$

12
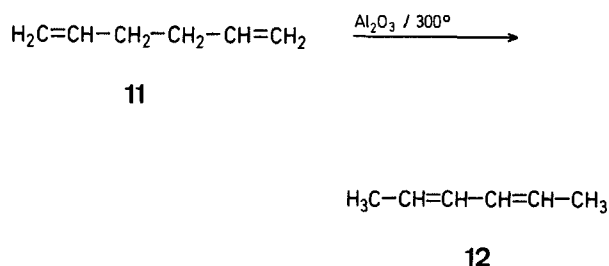
Another example of this reaction is the isomerization of 1,7-octadiene into the 3,5-isomer on a $Cr_2O_3-Al_2O_3$ catalyst[30].

The mode of preparation of and presence of other oxides in an alumina catalyst play an important role in determining its activity. Pure ®alumina gel catalyst B is reported to be very effective in inducing double bond shifts[31].

[17] V. Z. Sharf, L. K. Freidlin, E. N. German, G. I. Samokhvalov, Neftekhimiya 7, 57 (1967); C. A. 67, 21274 (1967).

[18] V. A. Dzisko, M. Kolovertnova, N. S. Kotsarenko, Kinetica i Kataliz 7, 508 (1966); C. A. 65, 9794 (1966).

[19] R. Y. Levina, A. A. Fainzilberg, V. M. Tatevzkii, E. G. Treshchova, Zh. Obshch. Khim. 21, 233 (1951); C. A. 45, 6990 (1951).

[20] Y. G. Mamedaliev et. al., Doklady Akad. Nauk Azberbaidzhan SSSR 11, 675 (1955); C. A. 50, 11934 (1956).

[21] S. Landa, L. Markovec, Collect. Czech. Chem. Comm. 29, 2309 (1964).

[22] W. W. McCarthy, J. Turkevich, J. Chem. Phys. 12, 405, 461 (1944).

The catalytic activity of alumina may generally be improved by the addition to it of various oxides (e.g., Cr_2O_3). Acids may also be used for this purpose, but the acid-treated catalysts tend to favor skeletal rearrangements. Fluorinated alumina catalyzes the skeletal isomerization of butene, whereas γ-alumina isomerizes 1-butene without skeletal rearrangement[32].

Supports other than Al_2O_3 are also effective as isomerization catalysts (see Section 3). Silica gel—already an active catalyst[21]—may be rendered even more active for the isomerization of 1-hexene by irradiation with neutrons[33]. Zeolites have also been studied. It was found that NaX- and Ni—NaX-zeolites catalyze (at 165–205° and 200–240°, respectively) the dehydration of 2-hydroxybutene to yield 1-butene; this initial product isomerizes to 2-butene at increased contact times[34].

Using zinc and magnesium silicates as catalyst in the range of 300–500°, the isomerization of 1-pentene yields predominantly 2-pentene[35]; some rearrangement of the carbon skeleton yielding small amounts of dienes and pentane isomers is also observed. Zinc chloride on alumina has also been used in the isomerization of 1-pentene at 350°; a mixture of C_5-hydrocarbons and condensation products was obtained[36]. The isomerization of the three butenes using metal sulfates on silica gel at ~60° yields a high ratio trans-2-butene : 1-butene[37]. Zinc and zinc chloride have also been found to effect double-bond migration in olefins under certain conditions[38].

1.1.3. Isomerization of linear olefins via hydroboration or by use of trialkylboranes, metals, complex metal hydrides, or metal complexes

Isomerizations of olefinic double bonds via hydroboration[39] or by use of complex metal hydrides proceed through an addition-elimination sequence.

Hydroboration of olefins, leading to their "contra-thermodynamic" isomers, is extremely useful for the preparation of α-olefins[39]:
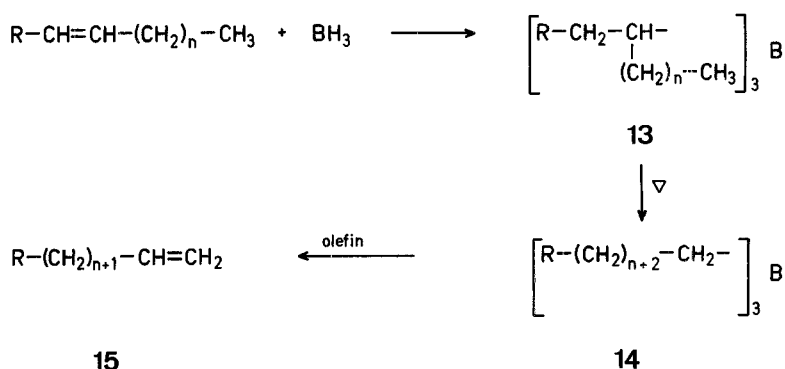
In such isomerizations, the boron atom freely migrates along the carbon chain of the intermediate organoborane (13) and ends up at the least hindered position (14). The reaction of organoborane 14 with further starting olefin, or with a second, "displacing", olefin liberates the desired terminal olefin 15. The reaction is driven to completion by using a large concentration of the displacing olefin, which is chosen so as to be less volatile than the desired terminal olefin, by distilling the terminal olefin out of the reaction mixture, and by using a displacing olefin which forms a very stable organoborane. All these methods have been applied and are well documented[39]. Organoboranes of olefins such as 1-pentene, 1-hexene, 3-methyl-1-butene, and 3-ethyl-1-pentene require approximately 6–8 hours for essentially complete displacement. The products are 90 to 95% pure terminal olefins, with 5–10% of the 2-alkene. No skeletal rearrangements have been observed in such isomerizations.

Isomerization of 2-octene by hydroboration[41]: In a 200-ml round-bottomed flask, a mixture of triglyme (50 ml) and 2-octene (40 ml) is treated with diborane (15 mmol) to form a catalytic amount of organoborane. The reaction mixture is then heated under reflux for 12 hr under a nitrogen atmosphere and subsequently fractionated using a Todd column. The distillate of b.p. 120–121° represents 22.9 g of olefin, contaning 28% 1-octene as indicated by I.R. analysis.

Trialkylboranes such as triethylborane have been shown[41] to catalyse the isomerization of olefinic double bonds in molecules in which no terminal double bond can be formed at 160–200°. This equilibrium reaction affords all the positional isomers of the starting olefin, e.g. 16:

$$R-(CH_2)_5-CH=CH-(CH_2)_5-R$$
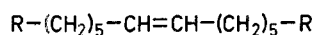
16

(R = C_6H_5 or substituted phenyl)

Any reaction preference for the isomer in which the double bond is conjugated with the phenyl ring much depends on the substitution of the aromatic ring: the presence of eletron-releasing groups on it

$$R-CH=CH-(CH_2)_n-CH_3 \ + \ BH_3 \longrightarrow \left[\begin{array}{c} R-CH_2-CH- \\ | \\ (CH_2)_n-CH_3 \end{array} \right]_3 B$$

13

$\downarrow \nabla$

$$R-(CH_2)_{n+1}-CH=CH_2 \xleftarrow{\text{olefin}} \left[R-(CH_2)_{n+2}-CH_2- \right]_3 B$$

15   **14**

[23] B. A. Kazanskii, I. V. Gostunskaya, N. B. Dobroserdova, Doklady Akad. Nauk SSSR **130**, 82 (1960); C. A. **54**, 10825 (1960).

[24] H. H. Voge, N. C. May, J. Amer. Chem. Soc. **68**, 550 (1946).
[25] P. J. Lucchesi, D. L. Baeder, J. P. Longwell, J. Amer. Chem. Soc. **81**, 3235 (1959).

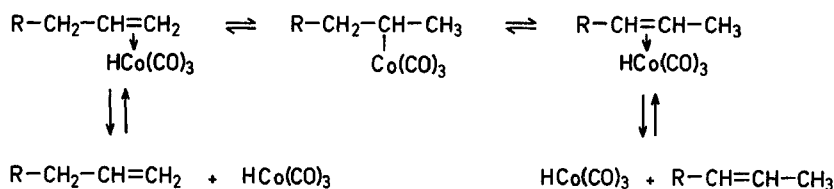increases slightly the preference for the conjugated isomer. Steric effects are very important. For instance, in the case of R=mesityl, overlap of the π-orbitals of the double bond and the aromatic ring is impossible for steric reasons; thus, the product contains a statistical distribution of the isomers.

The reaction mechanism involves the formation of small amounts of the organoborane derived from the olefin, e.g. 16, by exchange with the trialkylborane, e.g. triethylborane. The subsequent isomerization probably proceeds by a "slippering"[42] of the boron atom via intramolecular B—H bonds along the chain[43].

The isomerization of olefins in the presence of metal complexes has been thoroughly investigated and is well reviewed by Orchin[44] and Bond [45]. These investigations are of considerable importance in developing and understanding hydroformylation of olefins.

The isomerizations of olefins using a hydrogentetracarbonylcobalt [HCo(CO)₄] catalyst has been studied extensively[44]; allylbenzene, for example, is readily isomerized into propenylbenzene[46].

The following mechanisms for the process have been proposed. Hydrogentricarbonylcobalt was considered to be the double bond isomerizing agent in stoichiometric hydroformylation, in which the migration of the double bond[47] proceeds by an addition-elimination sequence:

ylbenzene only involves a nominal transfer of deuterium to the propenylbenzene. Thus, the D—Co-bond is not cleaved in the rate-determining step. When 1-octene containing tritium in the allyl position is isomerized with hydrogentetracarbonylcobalt in decane, the tritium label is not transferred to unlabelled 1-hexene also present in the mixture[48].

These observations have been rationalized as follows[48]. Two possible hydrogen shifts can take place separately or simultaneously in the π-complex of 16.

One of these, from metal to carbon, forms the basis of the mechanism proposed by Heck and Breslow[47]. The other, from carbon to carbon, represents a fast migration of the allyl hydrogen atom via a π-allyl complex. The allyl hydrogen in the latter case is much more mobile than the hydrogen bonded to metal. Thus, the latter mechanism is probably predominate in the case of olefins containing an allyl hydrogen atom, e.g., allylbenzene, whereas simple olefins like 1-octene are predominantly isomerized by hydrogen transfer from metal to carbon.

During the isomerization of a mixture of 1-octene tritiated in the allyl position and unlabelled 1-undecene or 1-hexene, using photoactivated pentacarbonyliron or thermally activated enneacarbonyldiiron as catalyst, non-transfer of tritium from the octene to the unlabelled olefin was observed[48]. Thus, the isomerization unequivocally takes place intramolecularly through a metal-olefin π-complex.

$$R-CH_2-CH=CH_2 \rightleftharpoons R-CH_2-CH-CH_3 \rightleftharpoons R-CH=CH-CH_3$$
$$\quad\;\; HCo(CO)_3 \qquad\qquad\quad Co(CO)_3 \qquad\qquad\quad HCo(CO)_3$$

$$\updownarrow \qquad\qquad\qquad\qquad\qquad\qquad\qquad \updownarrow$$

$$R-CH_2-CH=CH_2 + HCo(CO)_3 \qquad\qquad HCo(CO)_3 + R-CH=CH-CH_3$$

It was observed[46], however, that the DCo(CO)₄-catalyzed isomerization of allylbenzene into propen-

In the analogous isomerization using octacarbonyldicobalt as catalyst[47,48], only a small amount of

[26] J. W. HIGHTOWER, W. K. HALL, J. Amer. Chem. Soc. 89, 778 (1967).

[27] S. BIELIKOFF, J. FRAISSARD, B. IMELIK, Bull. Soc. Chim. France 1967, 3271.

[28] V. S. FELDBLYUM, G. P. KOMISAROVA, T. A. TSAILINGOLD, Kinetica i Kataliz 7, 175 (1966); C. A. 64, 17377 (1966).

[29] A. F. PLATE, M. I. BATUEV, Doklady Akad. Nauk SSSR 59, 1305 (1948); C. A. 42, 7234 (1948).

[30] R. Y. LEVINA, E. A. VIKTOROVA, Vestnik Moskov Univ. 6, no. 2, Ser. Fiz.-Mat. i Estestven. Nauk no. 1, 89 (1951); C. A. 46, 8605 (1952).

[31] A. C. OBLAD, J. V. MESSENGER, H. T. BROWN, Ind. Eng. Chem. 39, 1462 (1947).

[32] L. K. FREIDLIN, V. Z. SHARF, G. I. SAMOKHVALOV, E. N. GERMAN, Neftekhimiya 6, 887 (1966); C. A. 66, 85253 (1967).

[33] P. B. WEISZ, E. W. SWEGLER, J. Chem. Phys. 23, 1567 (1955).

[34] Z. V. GRYAZNOVA et al., Izv. Akad. Nauk SSSR, Ser. Khim. 1968, 1135; C. A. 69, 76244 (1968).

[35] N. I. SHUIKIN, V. A. TULUPOV, Zh. Obshch. Khim. 27, 1448 (1957); C. A. 52, 2730 (1958).

[36] N. I. SHUIKIN, N. A. POZDNYAK, Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk 1959, 1088; C. A. 54, 1260 (1960).

[37] M. MISONO, Y. SAITO, Y. YONEDA, J. Catalysis 9, 135 (1967).

[38] S. WAKAYAMA, J. Soc. Chem. Ind. Japan 50, 116 (1947).

[39] H. C. BROWN, Hydroboration. W. A. Benjamin Inc., New York, 1962.

[40] H. C. BROWN, B. C. SUBBA RAO, J. Amer. Chem. Soc. 81, 6437 (1959).

[41] A. J. HUBERT, J. Chem. Soc. [C] 1967, 235.

[42] R. E. WILLIAMS, J. Inorg. Chem. 1, 971 (1962).

[43] For a related type of isomerization (1,3-diphenylpropene and methyleneazomethines), see: S. PATAI, The Chemistry of Alkenes, Interscience Publishers, New York-London, 1964, p. 419

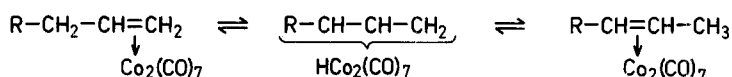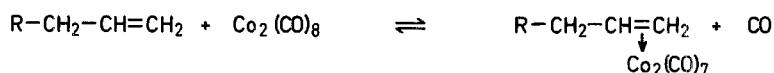[44] M. ORCHIN, Advan. Catalysis 16, 1 (1966); and references therein.

[45] G. C. BOND, Ann. Reports Chem. Soc. London 63, 27 (1966).

[46] L. ROOS, M. ORCHIN, J. Amer. Chem. Soc. 87, 5502 (1965).

[47] R. F. HECK, D. S. BRESLOW, J. Amer. Chem. Soc. 83, 4023 (1961).

[48] B. FELL, P. KRINGS, F. ASINGER, Chem. Ber. 99, 3688 (1966).

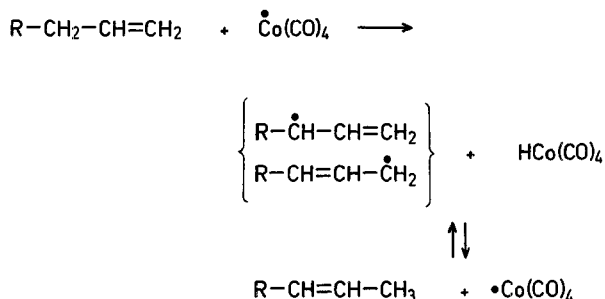tritium exchange is observed, and it is also proposed here that a fast intramolecular isomerization takes place:

$$R-CH_2-CH=CH_2 \ + \ Co_2(CO)_8 \ \rightleftharpoons \ R-CH_2-\underset{\underset{Co_2(CO)_7}{\downarrow}}{C}H=CH_2 \ + \ CO$$

$$R-CH_2-\underset{\underset{Co_2(CO)_7}{\downarrow}}{C}H=CH_2 \ \rightleftharpoons \ \underbrace{R-CH-CH-CH_2}_{HCo_2(CO)_7} \ \rightleftharpoons \ R-\underset{\underset{Co_2(CO)_7}{\downarrow}}{C}H=CH-CH_3$$

The olefin first forms a π-complex with the metal carbonyl. Fast intramolecular hydrogen shifts *via* the allyl π-complex then take place. Finally, a state of thermodynamic equilibrium is reached, without the olefin at any time having left the complex as would have been the case in an elimination-addition process.

Treatment of the final complex with a second, "displacing" olefin, preferably an α-olefin, or simple destruction of the complex itself affords the isomerized olefin usually in the *trans*-configuration.

The observed tritium exchange takes place through a side reaction involving $Co(CO)_4$-radicals formed by thermal cleavage of the octacarbonyl-dicobalt. The reaction mechanism is very similar to that of the iodine-catalyzed isomerization of double bonds:

$$R-CH_2-CH=CH_2 \ + \ \overset{\bullet}{C}o(CO)_4 \ \longrightarrow$$

$$\left\{\begin{array}{l} R-\overset{\bullet}{C}H-CH=CH_2 \\ R-CH=CH-\overset{\bullet}{C}H_2 \end{array}\right\} \ + \ HCo(CO)_4$$

$$\Updownarrow$$

$$R-CH=CH-CH_3 \ + \ \bullet Co(CO)_4$$

It was reported recently[50] that the compound $[Co(CO)_2PR_3]_3$ is a very active catalyst for the isomerization of pentenes at 60°.

Derivates of cobalt have been most widely investigated with relation to their use as hydroformylation catalysts; however, other metal derivatives have also been found to be active catalysts for olefin isomerization. Thus, $[HFe(CO)_4]^{\ominus}$ in ether at room

temperature catalyzes the isomerization of 1-hexene to 2- and 3-hexene (90% after 24 hours)[51]. The catalytic properties of this iron complex were earlier predicted[51] and can be explained on the basis of the existence of a dimeric ion (17) formed from two $[HFe(CO)_4]^{\ominus}$ ions, which decomposes into the complex 18 and hydrogen:

$$2\left[HFe(CO)_4\right]^{\ominus} \ \longrightarrow \ \left[(CO)_3FeH\underset{\underset{O}{\overset{\overset{O}{\parallel}}{C}}}{\overset{\overset{O}{\overset{\parallel}{C}}}{\diagup\diagdown}}HFe(CO)_3\right]^{\ominus\ominus}$$

17

$$\longrightarrow \ \left[(CO)_3Fe\underset{\underset{O}{\overset{\overset{O}{\parallel}}{C}}}{\overset{\overset{O}{\overset{\parallel}{C}}}{\diagup\diagdown}}Fe(CO)_3\right] \ + \ H_2$$

18
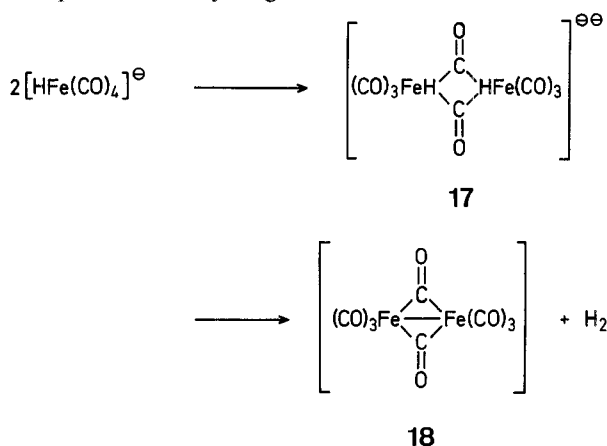
The structural resemblance between 18 and dicobalt octacarbonyl makes clear the catalytic activity of the former.

Other iron carbonyls[44,52,53,54] are also active catalysts for the double bond isomerization of olefins. The mechanism very probably involves a similar type of π-complex to that discussed in the case of the cobalt carbonyls. For instance, $Fe(CO)_5$ isomerizes 3-phenylallyl alcohol to 3-phenylpropanol[55]. It has been shown[56] that the catalytic activity of pentacarbonyliron is greatly enhanced by U.V. irradiation of the reaction mixture, probably because this facilitates formation of the complex 18. Other metal carbonyls (e.g., of osmium and manganese)[56] are also more or less active catalysts for the isomerization of double bonds.

[49] F. ASINGER, O. BERG, Angew. Chem. 61, 266 (1946).

[50] G. PREGAGLIA, A. ANDREETTA, G. FERRARI, R. UGO, Chem. Commun. 1969, 590.

[51] H. W. STERNBERG, R. MARKBY, I. WENDLER, J. Amer. Chem. Soc. 78, 5704 (1956).

[52] T. A. MANUEL, Trans. N. Y. Acad. Sci. 26, 442 (1964).

[53] T. A. MANUEL, J. Org. Chem. 27, 3941 (1962).

[54] G. WILKE et al., Angew. Chem. 78, 157 (1966); Angew. Chem., Intern. Edit. 5, 151 (1966).

[55] French Pat. 1423128 (1966) S. F. CHAPPELL, C. E. SIBERT; (Columbian Carbon Co.); C. A. 65, 10514 (1966).

[56] F. ASINGER, B. FELL, K. SCHRAGE, Chem. Ber. 98, 372 (1965).

[57] M. UCHINO, Y. CHAUVIN, G. LEFEBVRE, C. r. Acad. Sci. Paris [C] 265, 103 (1967).

[58] E. W. STERN, Advan. Catalysis 16, 108 (1966).

[59] see, for example: R. HÜTTEL, Synthesis 1970, 225.

[60] F. ASINGER, B. FELL, P. KRINGS, Tetrahedron Letters 1966, 633.

[61] N. R. DAVIES, Austral. J. Chem. 17, 212 (1964); and references therein.

[62] E. W. STERN, Catal. Rev. 1, 73 (1967).

[63] I. I. MOISEEV, S. V. PESTRIKOV, Izv. Akad. Nauk SSSR, Ser. Khim. 1965, 1717; C. A. 63, 17835 (1965).

[64] I. I. MOISEEV, S. V. PESTRIKOV, L. M. SVERZH, Izv. Akad. Nauk SSSR, Ser. Khim. 1966, 1866; C. A. 66, 64859 (1967).

Nickel π-complexes in combination with Lewis acids[54] or salts of nickel in combination with an organoaluminum compound[57] are also effective isomerization catalysts.

Noble metal chlorides and complexes represent another class of isomerization catalysts for olefinic double bonds[45,59]. Comparative studies of the isomerization of n-octenes with $PdCl_2$, $RhCl_3$, and $PtCl_2$ have been carried out[58].

The industrial importance of processes for the conversion of ethylene into acetaldehyde or into vinyl-acetate using palladium(II)-chloride catalysis has stimulated enormous interest in the mechanisms of these and other reactions of noble metal salts with olefins. Practically all the heavy transition metals catalyze olefin isomerization[44]. Asinger et al.[60] showed that isotopic exchange (intramolecular hydride transfer) takes place during the $PdCl_2$, $RhCl_3 \cdot 3H_2O$, and $PtCl_2$-catalyzed isomerizations of 1-octene containing tritium in the allyl position when unlabelled 1-hexane is present. The stereoselectivity of these reactions, particularly when only a low degree of isomerization is achieved, which lead to cis-2-olefin formation in a "contrathermodynamic" process, also points toward the hydride-transfer mechanism. The catalytic activity of palladium(II)-chloride can be increased by dissolving it in dilute hydrochloric acid and evaporating the solution. The palladium(II)-chloride thus obtained is, in contrast to the non-activated species, soluble in hexene and octene. This activated palladium(II)-chloride isomerizes 2-methyl-1-pentene and 4-methyl-1-pentene to the equilibrium mixture of 2-methylpentenes, in contrast to the observation[61] that 2-methyl-1-pentene can not be isomerized with non-activated palladium(II)-chloride. Thus, the carbene mechanism[61] postulated must be incorrect.

The isomerization reactions with palladium(II)-chloride can be carried out in a pure olefin or using a variety of nonpolar and polar solvents[62]. They are

not accompanied by skeletal isomerization if the reaction is carried out under suitable conditions. Precipitation of palladium is occasionally observed, but the extent of isomerization is not proportional to the amount of metal deposited.

Such deposition of metal can be avoided if nucleophilic substances are absent from the reaction medium or the reaction conditions are chosen so that nucleophilic reactions are suppressed. The thorough drying of reagents and apparatus is also essential. The following derivatives of palladium have been used as double bond isomerization catalysts:

$PdCl_2$, Li_2PdCl_4, Na_2PdCl_4, $(C_6H_5CN)_2PdCl_2$, $(CH_3CN)_2$, Pd-salicylate, and olefin-$PdCl_2$ π-complexes. It has been reported[63,64] that the system $PdCl_2$-$HClO_4$ isomerizes 1-butene into 2-butene via a complex containing a Pd—Pd bond.

Complexes of platinum and iridium are generally not very active in the isomerization of olefins. It has, however, been found that platinum complexes containing triphenylphosphine, triphenylarsine, or triphenylstibine as ligands are effective catalysts[65]. The fact that the system Pt^{II}—Sn^{II} promotes room-temperature isomerization of 1-pentene is particularly interesting, as this represents an example of the enhancement of the catalytic effect of Pt^{II} alone by a second metal[45,66].

Iridium[III]-phosphine complexes catalyze the migration of the double bond in octenes[45], whereas iridium(III)-chloride requires a co-catalyst to activate it[45].

Much study has been devoted to the use of rhodium catalysts for the isomerization of olefins, particularly the so-called "Wilkinson catalyst" L_3RhCl (L = triphenylphosphine). The mechanism which has been proposed[67] for such reactions (see following scheme) explains the fact that in the isomerization of butene in the presence of deuterium chloride, part of the 1-butene obtained is deuterated whereas the 2-butene in the product contains practically no deuterium.

[65] J. C. BAILAR, H. ITATANI, J. Amer. Chem. Soc. 89, 1592 (1967).

[66] G. C. BOND, M. HELLIER, J. Catalysis 7, 217 (1967).

[67] R. CRAMER, Accounts Chem. Res. 1, 186 (1968).

[68] R. CRAMER, J. Amer. Chem. Soc. 88, 2272 (1966).
R. CRAMER, R. V. LINDSAY, J. Amer. Chem. Soc. 88, 3534 (1966).

[69] J. F. HARROD, A. J. CHALK, J. Amer. Chem. Soc. 88, 3491 (1966).

[70] H. WAKAMATSU, Nippon Kagaku Zasshi 85, 227 (1964); C. A. 61, 13173 (1964).

[71] D. EVANS, J. A. OSBORN, G. WILKINSON, J. Chem. Soc. [A] 1968, 3133.

[72] G. J. K. ACRES, G. C. BOND, B. J. COOPER, J. A. DAWSON, J. Catalysis 6, 139 (1966).

[73] R. CRAMER, J. Amer. Chem. Soc. 89, 1633 (1967).

[74] W. D. HUNTSMAN, N. L. MADISON, S. I. SCHLESSINGER, J. Catalysis 2, 498 (1962).

[75] M. DUBINI, F. MONTINO, Chim. Ind. (Milano) 46, 793 (1964).

[76] G. H. TWIGG, Proc. Roy. Soc. (London) [A] 178. 106 (1941).

[77] I. V. GOSTUNSKAYA et al., Neftekhimiya 7, 3 (1967); C. A. 67, 21276 (1967).

[78] G. G. EBERHARDT, L. VASKA, J. Catalysis 8, 183 (1967).

[79] R. Y. LEVINA, D. A. PETROV, Zh. Obshch. Khim. 7, 747 (1937); C. A. 31, 5772 (1937).

[80] R. Y. LEVINA, Zh. Obshch. Khim. 6, 1092 (1936); C. A. 31, 1002 (1937).

[81] J. I. MACNAB, G. WEBB, J. Catalysis 10, 19 (1968).

[82] S. CARRA, V. RAGAINI, J. Catalysis 10, 230 (1968).

[83] R. NICOLOVA, D. BARTHOLOMEUF, H. CHARCOSSET, Y. TRAMBOUZE, C. r. Acad. Sci. Paris [C] 265, 468 (1967).

[84] R. MAUREL, M. GIUSNET, M. MARCO, J. E. GERMAIN, Bull. Soc. Chim. France 1966, 3082.

[85] W. G. YOUNG et al., J. Amer. Chem. Soc. 69, 2046 (1947).

[86] L. HORNER, I. GROYMANN, Liebigs Ann. Chem. 670, 1 (1963).

[87] A. SCHINDLER, Makromol. Chem. 90, 284 (1966).

This mechanism also accounts for the stereospecific production of *trans*-butene-2-*d* in the isomerization of *cis*-2-butene with a RhD catalyst[67,68]:
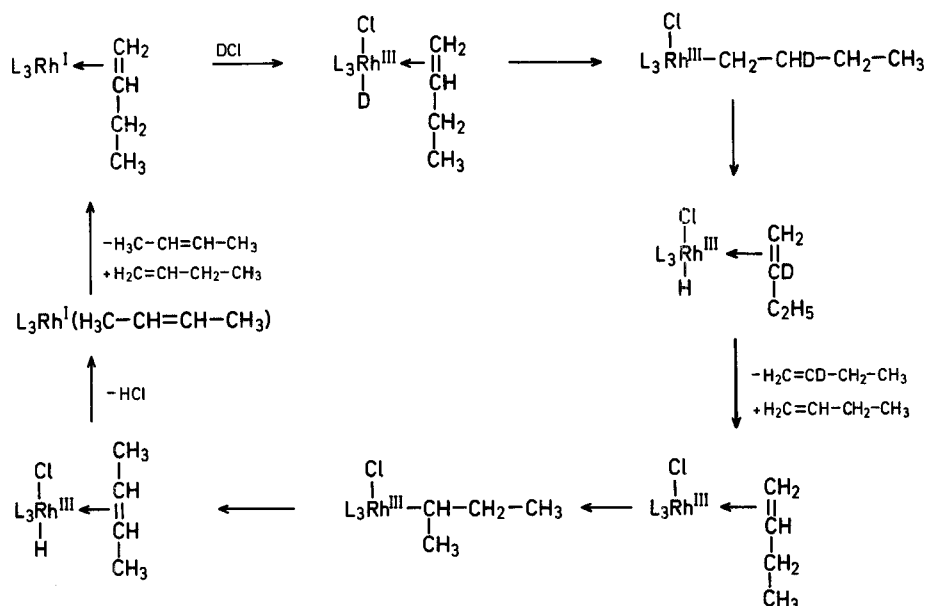
olefin remaining in the reaction mixture contained exclusively the internal isomers. These facts suggest that there are two different kinds of active sites in the

$$L_3Rh^I \leftarrow \begin{array}{c} CH_2 \\ \| \\ CH \\ | \\ CH_2 \\ | \\ CH_3 \end{array} \xrightarrow{DCl} L_3Rh^{III} \leftarrow \begin{array}{c} Cl \\ | \\ \| \\ D \\ | \\ CH_2 \\ | \\ CH_3 \end{array} \longrightarrow L_3Rh^{III}-CH_2-CHD-CH_2-CH_3$$

$$\uparrow \begin{array}{c} -H_3C-CH=CH-CH_3 \\ +H_2C=CH-CH_2-CH_3 \end{array}$$

$$L_3Rh^I(H_3C-CH=CH-CH_3)$$

$$\uparrow -HCl$$

$$L_3Rh^{III} \leftarrow \begin{array}{c} Cl \\ | \\ \| \\ CH \\ | \\ H \end{array} \begin{array}{c} CH_3 \\ | \\ CH \\ \| \\ CH \\ | \\ CH_3 \end{array} \longleftarrow L_3Rh^{III}-\begin{array}{c} Cl \\ | \\ CH-CH_2-CH_3 \\ | \\ CH_3 \end{array} \longleftarrow L_3Rh^{III} \leftarrow \begin{array}{c} Cl \\ | \\ CH_2 \\ \| \\ CH \\ | \\ CH_2 \\ | \\ CH_3 \end{array}$$

$$L_3Rh^{III} \leftarrow \begin{array}{c} Cl \\ | \\ CH_2 \\ \| \\ CD \\ | \\ H \end{array} C_2H_5$$

$$\downarrow \begin{array}{c} -H_2C=CD-CH_2-CH_3 \\ +H_2C=CH-CH_2-CH_3 \end{array}$$

Thus, in contrast to some palladium catalysts (e. g., dibenzonitrile-palladium dichloride), which isomerize *via* π-allyl complexes (1,3-hydrogen migrations), the rhodium catalyst isomerizes olefins through rapid reversible additions of hydride[67,69].

Rhodium carbonyl catalyzes the migration of the double bond in 1-butene[70]. The complex **19** is an efficient catalyst for the isomerization of 1-pentene into 2-pentene (90% yield)[71]:

RhCl(CO)[P(C₆H₅)₃]₂   **19**
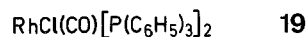
Rhodium trichloride on silica gel in ethylene glycol as solvent has been reported to be an effective catalyst for the isomerization of the double bond in olefins[72].

Surprisingly, 1,4-hexadiene was obtained by treatment of a mixture of ethylene and butadiene with rhodium(III)-chloride. Using the same catalyst, this diene is isomerized into the conjugated isomer (stereoisomers of 2,4-hexadiene)[73]. The catalyst also isomerizes 1-butene rapidly at room temperature; the isomerization is inhibited by 1,3-butadiene. Formation of a stable allyl π-complex of Rh^III and butadiene could explain this latter effect.

1.1.4. Isomerization of linear olefins by hydrogenation- and Ziegler-Natta-type catalysts

A study of the racemization of olefins during their hydrogenation[74] revealed that this is due to isomerization of their double bonds. Addition of bases to the reaction mixture caused a reduction in the rate of hydrogenation and an even greater decrease in the rate of double bond migration. The alkane formed was not racemized, but the unhydrogenated

catalyst, one (which can be deactivated by bases) being very active in hydrogenation and simultaneously in migration of double bonds, and the other being only weakly active or inactive in the migration of double bonds but quite highly active in catalyzing the hydrogenation of terminal alkenes (but not internal double bonds).

The isomerization of double bonds on catalysts such as Ni, NiCl₂, Ni—Fe, Pd/BaSO₄, PdCl₂, Pd—Fe, and Pt occurs through a mechanism involving a metal-hydrogen bond and appears to be independent of the hydrogenation reaction[75].

In the presence of hydrogen, nickel catalyzes the isomerization of 1-butene to 2-butene[76]. It has been suggested[10] that a concerted mechanism is operative in the nickel-catalyzed migration of double bonds, as the Ni—Ni distance in the crystal lattice is 3.52 Å. Therefore, a mechanism similar to that described in Section 1.1.3. for isomerization *via* hydroboration, involving a species such as NiH—Ni, could be operative.

The following order of activity of catalysts for the isomerization of hexenes has been observed[77]:

$$Pd > Ni > Rh \geqslant Rn > Os \approx Ir \approx Pt.$$

The simultaneous hydrogenation and isomerization of 1-butene is catalyzed by *trans*-chlorocarbonyl-bis-[triphenylphosphine]-iridium in the presence of hydrogen[78].

⁶⁸ N. V. Obeschchalova, V. S. Feldblyum, M. E. Basner, V. S. Dzyuba, Zh. Org. Khim. **4**, 574 (1968); C. A. **68**, 113778 (1968).

Noble metal catalysts on various supports have been widely used for the isomerization of olefins. Alumina[52,55,58,60], silica[52], and active carbon[79,80] are generally used as supports. Thus, butene may be isomerized by rhodium on silica[81], rhodium on alumina, palladium on alumina[82], and platinum on alumina[83]. The isomerization of 2,3-dimethyl-1-butene to 2,3-dimethyl-2-butene is effected by the metals Pt, Pd, Ni, Co, or Cu on an alumina support[84]. The migration of the double bond is probably due to both the catalytic action of the metal and of the acidic sites of the support[83].

The product equilibrium of the various butenes can be reached on hydrogenation catalysts such as palladium on barium sulfate[85].

cis-trans-Isomerization of olefins with migration of the double bond has been found to occur to a greater extent when using palladium and Raney nickel as catalysts than in the presence of platinum[86].

The isomerization 20 → 21 was observed[79] at 300° on Pt/C:
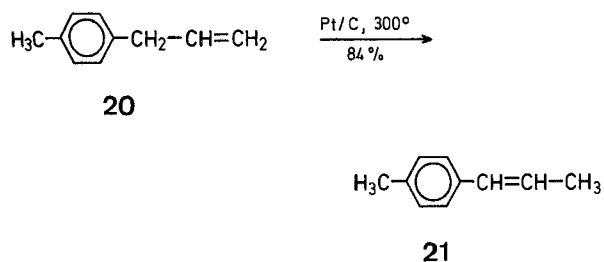
Isomerization of two isolated double bonds into conjugation takes place on Pd/asbestos or on Pt/C[80]:
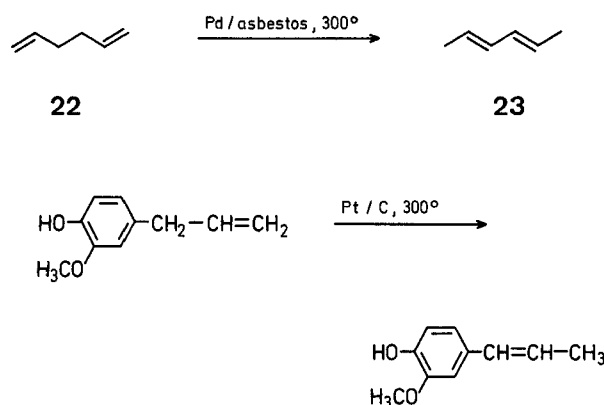
Isomerization of olefinic double bonds has also been very frequently observed with Ziegler-Natta catalysts[87,88,89,90]. The system CH_3TiCl_3—CH_3AlCl_2 catalyzes the isomerization of 1-olefins into 2-olefins, whereby the cis isomer is formed preferentially[91]. The $(C_2H_5)_3Al_2Cl_3$-bis[t-butylbenzoate]-nickel complex is a very active isomerization catalyst for olefins[88]. A study of the skeletal rearrangement of 1,4-dienes on (tributylphosphine)$_2$NiCl$_2$/(isobutyl)$_2$AlCl, revealed that this catalyst is also effective in the isomerization of double bonds[92]. The catalyst iron-ethyl hexanoate–triethylaluminium isomerizes[93] 1-hexene to a mixture of cis-2-hexene (72%) and cis- and trans-3-hexene (72%).

The same kind of isomerization also takes place on titanium(III)-chloride. The system titanium(III)-chloride/palladium(II)-chloride was the subject of a study of mobile isomerization equilibria with relation to the polymerization of olefin mixtures[94].

1.1.5. Thermal isomerizations of linear olefins

Although a thermal isomerization of a linear olefin was reported more than 50 years ago[95], detailed mechanistic studies of such reactions have only been carried out during recent years.

In a 1,5-hydrogen transfer, ocimene (24) isomerizes at 200° to alloöcimene (25)[95,96,97]:
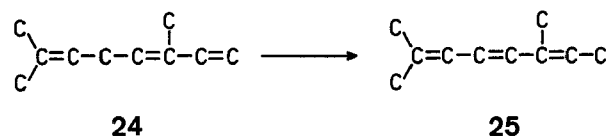
The mechanism of this type of isomerization has recently been investigated[98] in the case of cis-2-methyl-1,3-pentadiene (26). The thermodynamic parameters were determined and it was proposed that the equilibrium between 26 and 29 is established via a cyclic transition state 27 or 28. The enthalpy difference (ΔH) between 26 and 29 is −3.43 kcal/mole, and the equilibrium constant (K) is 10.79 at 229°.
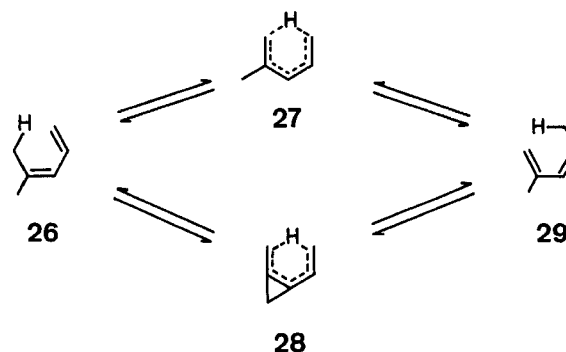
[89] D. W. AUBREY, A. BARNATT, W. GERRARD, J. Polym. Sci. [B] 3, 357 (1965).

[90] Y. CHAUVIN, G. LEFEBVRE, C. r. Acad. Sci. Paris 259, 2105 (1964).

[91] H. BESTIAN, K. CLAUSS, Angew. Chem. 75, 1070 (1963).

[92] R. G. MILLER, J. Amer. Chem. Soc. 89, 2785 (1967).
R. G. MILLER, T. J. KEALY, A. L. BARNEY, J. Amer. Chem. Soc. 89, 3756 (1967).

[93] French Patent 1403409 (1963) S. J. LAPPORTE (California Research Corp.); C. A. 63, 14725 (1965).

[94] N. H. PHUNG, Y. CHAUVIN, G. LEFEBVRE, Bull. Soc. Chim. France 1967, 3618.

[95] C. J. ENKLAAR, Rec. Trav. Chim. 26, 171 (1907).

[96] J. WOLINSKY, B. CHOLLAR, M. D. BAIRD, J. Amer. Chem. Soc. 84, 2775 (1962).

[97] J. E. HAWKINS, H. G. HUNT, J. Amer. Chem. Soc. 73, 5379 (1951).

A transition state involving structure **28** is supported by the fact that the isomerization of 1-methyl-2-vinylcyclopropane[99] is best rationalized in terms of a similar intermediate.

The isomerization of hexadiene **30** at 490° in the gas phase to cis-, trans-2,4-hexadiene **(31)**[100] also occurs via a 1,5-shift:

30   **31**
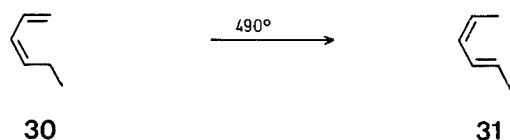
In addition, 2-ethyl-cis-1,3-pentadiene **(32)** is reversibly isomerized to 4-methyl-trans-1,3-hexadiene **(33)**; the equilibrium constant K (33/32) is 8.794 at 250° [101]:

32   **33**

The thermal equilibrium constants for many monoolefins have been published by the National Bureau of Standards[102].

1.1.6. Radical isomerization of linear olefins

The isomerization, probably radical-induced, of olefins during the oxidation of unsaturated compounds has been observed[103].

An extensive investigation of the migration of olefinic double bonds in the presence of nitric oxide and iodine at temperatures of about 250° showed that the reactions are probably of radical nature[104,105,106].

A convincing proof of the activity of radicals as catalysts for the isomerization of double bonds is the fact that mercury atoms isomerize 1-butene into 2-butene[107] at 30°.

The isomerization of terminal olefins by hydrogen bromide in the presence of light proceeds via the abstraction of an allylic hydrogen by a bromine radical followed by addition of a hydrogen atom to the terminal carbon atom[108].
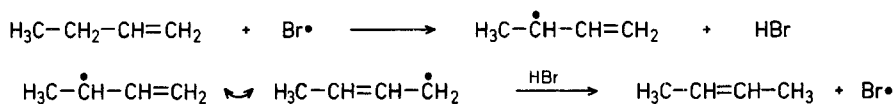
producing compounds such as diphenyl sulfide or diphenyl disulfide in cyclohexane effects cis-trans equilibration without migration of the double bond[110]. Similar results are obtained when photosensitizers are added to the reaction mixture containing the benzenethiyl radical-producing compounds and wavelengths of > 320 mμ are used; in this case, however, some migration $(2-3\%)$ of the double bond occurs. The equilibria found in these cis-trans isomerizations are close to the corresponding thermodynamic equilibria. Different results are obtained with systems in which the olefinic double bond is not isolated, e. g. stilbene.

1.2. Isomerization of Endocyclic and Exocyclic Olefins

1.2.1. Thermal isomerization of endocyclic and exocyclic olefins

The thermal isomerization of cyclic dienes is mechanistically particularly interesting because it demonstrates the existence of intramolecular hydrogen shifts (e. g., 1,5-hydrogen migrations). Such migrations in linear dienes have already been discussed in Section 1.1.5. One of the prerequisites for facile 1,5- (and 1,7-) hydrogen shifts is the formation of a transition state in which the hydrogen atom and the double bonds of the molecule are in a favorable spacial relationship for migration. The following representation of the transition state for the precalciferol-calciferol interconversion serves to illustrate this statement[111]:
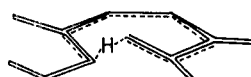
Transition State for the Precalciferol-Calciferol Interconversion

The 1,5-hydrogen shifts in C_6-, C_7-, C_8-, and C_9-membered rings have similar activation energies, whereas the activation energy for such migrations in the C_5-ring (cyclopentadiene) is exceptionally low[112].

Certain types of radicals catalyze cis-trans olefin isomerization without any double-bond migration[109,110]. Thus, irradiation of 2-butene, 2-pentene, and 5-decene with suitably filtered light (wavelength 300 mμ) in the presence of benzenethiyl radical-

$H_3C-CH_2-CH=CH_2$ + Br• $\longrightarrow$ $H_3C-\overset{\bullet}{C}H-CH=CH_2$ + HBr

$H_3C-\overset{\bullet}{C}H-CH=CH_2$ ⇌ $H_3C-CH=CH-\overset{\bullet}{C}H_2$ $\xrightarrow{\text{HBr}}$ $H_3C-CH=CH-CH_3$ + Br•

[98] H. M. FREY, R. J. ELLIS, J. Chem. Soc. **1965**, 4770.

[99] R. J. ELLIS, H. M. FREY, J. Chem. Soc. **1964**, 5578.

[100] H. M. FREY, B. M. POPE, J. Chem. Soc. [A] **1966**, 1701.

[101] H. M. FREY, R. K. SOLLY, J. Chem. Soc. [A] **1969**, 733.

[102] J. E. KILPATRICK et al., J. Research Natl. Bur. Standards **36**, 559 (1946); C. A. **40**, 6330 (1946).

[103] E. G. E. HAWKINS, Organic Peroxides, Their Formation and Reactions, Van Nostrand Co, Princeton, N. J., 1961, p. 35.

[104] K. W. EGGER, S. W. BENSON, J. Amer. Chem. Soc. **88**, 236 (1966).

[105] S. W. BENSON, A. N. BOSE, J. Amer. Chem. Soc. **85**, 1385 (1963). S. W. BENSON, A. N. BOSE, P. NANGIA, J. Amer. Chem. Soc. **85**, 1385 (1963).

[106] K. W. EGGER, S. W. BENSON, J. Amer. Chem. Soc. **88**, 236, 241 (1966).

[107] H. E. GUNNING, E. W. R. STEACIE, J. Chem. Phys. **14**, 581 (1946).

[108] P. I. ABELL, J. Amer. Chem. Soc. **88**, 1346 (1966).

[109] F. ASINGER, B. FELL, Erdöl und Kohle **19**, 500 (1966).

1.2.1.1. Thermal isomerization of five-membered cycloolefins

As just mentioned, 1,5-hydrogen shifts in cyclopentadienes and indenes are particularly facile. Thus, 5-methylcyclopentadiene (34) is isomerized into a mixture containing equal amounts of 35 and 36; the half-life of the reaction is 20 – 25 minutes in the liquid phase at 25 – 28° [113]:


34 <5%   **35** 50%   **36** 50%
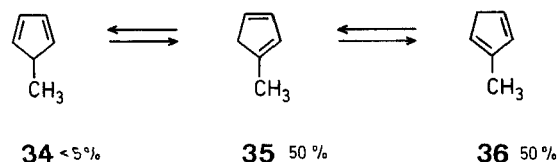
Under similar conditions, 1,5-dimethylcyclopentadiene affords 40% 2,3- and 60% 1,2-dimethylcyclopentadiene, whereas 1,3-dimethylcyclopentadiene and 1,4,5-trimethylcyclopentadiene gave 90% yields of the 1,3- and 1,2,3-isomers, respectively. In indene, a 1,3-hydrogen migration is favored because a 1,2-shift would give the non-aromatic system 38. However, the fact that there is a statistical distribution of deuterium in the product of the isomerization of 1-deuterioindene at 200° indicates that the isoindene (38) is, in fact, an intermediate [114,115]:

37   **38**   **39**
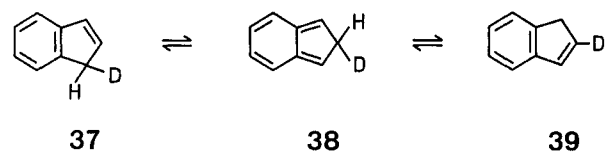
The difference in enthalpy between the 1,3-H shift in indene and the 1,5-H-migration in cyclopentadiene is about 11.5 kcal/mole [114].

The thermal isomerization of indene derivatives is also known. For example [116], 2,3-diphenylindene (46) gives 1,2-diphenylindene (47):

40   **41**
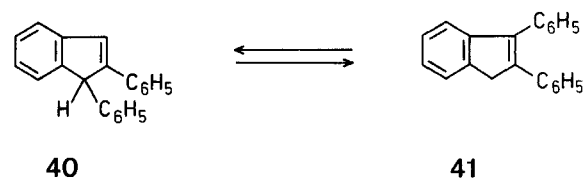
When both exo- and endo-products may be formed from the isomerization of a C₅-ring system, the endo isomer is favored [117,118,119]. Even in the case of benzylidenecyclopentane (42), the endo isomer 43 is the more stable [120,121]:

42   **43**
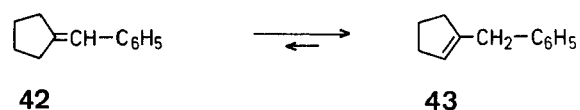
The isomerization of 44 into 45, via a 1,5-hydrogen transfer, takes place quantitatively at 360°. Such reactions, which only take place when the double bonds in the 1,3-diene system are in the cisoid configuration [96], can be used to differentiate between cisoid und transoid 1,3-dienes:

44   **45**
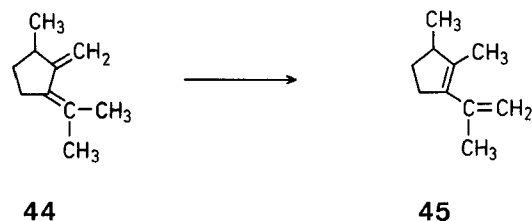
The requirement that a cisoid conformation be present is determined by the cyclic transition state of the rearrangement.

The bicycloheptene derivatives 46 are isomerized [122] at 285° into the exocyclic isomers 47:

46   **47**

$R^1 = R^2 = H; \quad R^1 = H, \quad R^2 = CH_3; \quad R^1 = R^2 = CH_3$
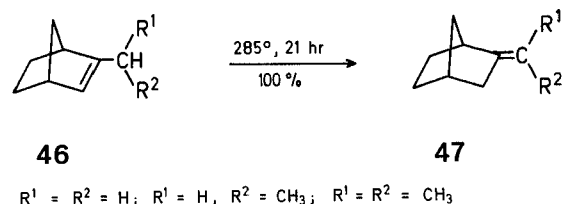
1.2.1.2. Thermal isomerization of six-membered cyclic olefins

The thermal migration of double bonds in substituted cyclohexadienes occurs at 300 – 400° [123,124]:

48   **49**   **50**   **51**

52   **53**
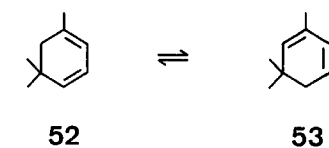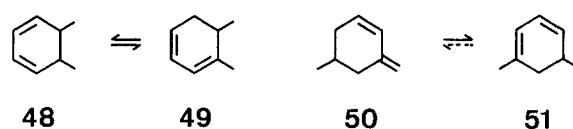
In the isomerization of 54 into 55 and of 56 into 57, 1,5-hydrogen shifts occur:

54   **55**

56   **57**
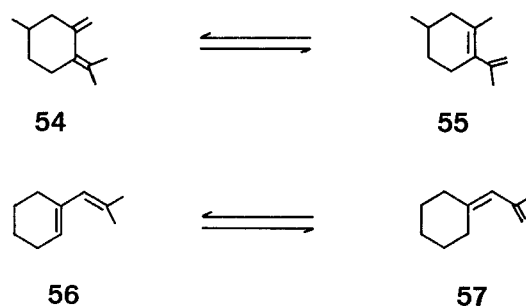
[110] C. MOUSSEBOIS, J. DALE, J. Chem. Soc. [C] 1966, 260.

[111] J. L. M. A. SCHLATMANN, J. POT, E. HAVINGA, Rec. Trav. Chim. 83, 1173 (1964).

[112] D. S. GLASS, R. S. BOIKESS, S. WINSTEIN, Tetrahedron Letters 1966, 999.

[113] V. A. MIRONOV, E. V. SOBOLEV, A. N. ELIZAROVA, Tetrahedron 19, 1939 (1963).

[114] W. R. ROTH, Tetrahedron Letters 1964, 1009.

1.2.1.3. Thermal isomerization of seven-membered cyclic olefins

Thermal isomerization of cycloheptadienes and cycloheptatrienes also takes place via intramolecular 1,5-hydrogen shifts. This mechanism was principally elucidated by kinetic studies on deuterium-labelled


65
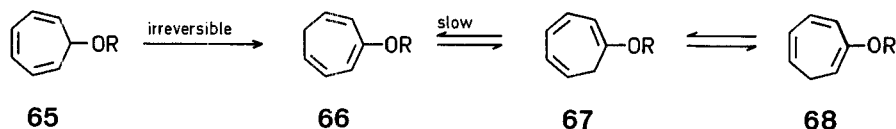
cycloolefins. A common observation in all these studies is the high negative value of the activation entropy, which indicates the rigid cyclic nature of the transition state. Thus, the isomerization[125] of deuteriocycloheptatriene (**58**) takes place via the transition state **59**:

58   **59**   **60**
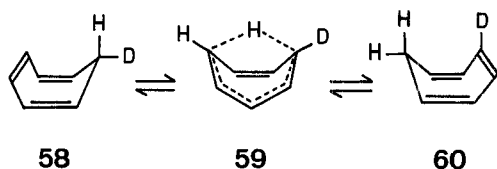
The nature of the hydrogen shifts observed with this type of catalyst are of interest in connection with the fact that cycloheptatrienecarboxylic acids are readily isomerized under basic conditions[126].

Cycloheptadiene (**61** − **64**) 1,5-hydrogen shifts have only very recently been reported[127]. They occur at 140 − 160°.

61   **62**   **63**   **64**
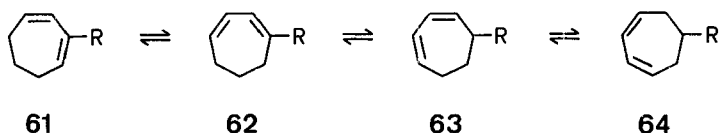
The thermal isomerization of cycloheptatrienes has been extensively studied[125,128,129]. The absence of a solvent effect on the rate of these isomerizations is in agreement with the proposed formulation of their common, multicenter transition state[130,131]. It has been shown that the photoisomerizations of 7-deuteriocycloheptatriene and of 7-phenylcyclo-heptatriene are intramolecular, as are the thermal reactions, but in the photoreactions, 1,7- and not 1,5-shifts were observed[128].

The rearrangement of 7-methyl-1,3,5-cyclohepta-triene proceeds in both the gas and the liquid phases via a 1,5-hydrogen shift[132].

Substituted members of the C_7 series also exhibit 1,5-hydrogen shifts[133,134]. For instance, isomerization of 7-methoxycycloheptatriene (**65**, R=CH_3) to **66** (R=CH_3) occurs irreversibly at 150°; subsequent reversible isomerization leads to an equilibrium mixture of **66** − **68** (R=CH_3)[135]:

66   **67**   **68**

The thermal isomerizations of 7-methoxy- (**65**, R=CH_3—) and ethoxy-(**65**, R=C_2H_5—) cyclohepta-trienes were studied using N.M.R. spectroscopy[136]. The compositions of the equilibrium mixtures at 195° were measured with the following results: For R=CH_3: 18% of **66**, 77% of **67**, and 4.6% of **68**; for R=C_2H_5: 15.2% of **66**, 84.8% of **67**, and 0% of **68**.

The isomerization of dihydrotropolone (**69**) at 60–100° takes place via a 1,5-hydrogen shift[131]:

69   **70**
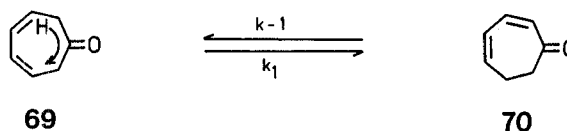
As expected, the presence of a phenyl group in the molecule alters the equilibrium in favor of the more conjugated isomer[137]:

71   **72**
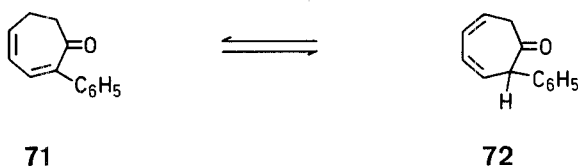
exo-endo-Isomerization of ethylidene cycloheptane (**73**) similar to that found in the 5-ring series has been observed[138]:

73   **74**

[115] K. ALDER, F. PASCHER, H. VAGT, Chem. Ber. **75**, 1501 (1942).
[116] C. F. KOELSCH, P. R. JOHNSON, J. Amer. Chem. Soc. **65**, 567 (1943).
[117] O. WALLACH, Liebigs Ann. Chem. **353**, 307 (1907).
[118] H. C. BROWN, J. Org. Chem. **22**, 439 (1957).
[119] Y. I. GOLDFARB, L. I. BELINKII, Uspechi Chimii **29**, 470 (1960); Russian Chem. Rev. **29**, 214 (1960).
[120] E. L. ELIEL, J. W. McCOY, C. C. PRICE, J. Org. Chem. **22**, 1533 (1957).

[121] H. J. SCHAEFFER, C. J. COLLINS, J. Amer. Chem. Soc. **78**, 124, 128 (1956).
[122] K. ALDER, H. J. ACHE, Chem. Ber. **95**, 511 (1962).
[123] H. PINES, R. H. KOZLOWSKI, J. Amer. Chem. Soc. **78**, 3776 (1956).

## 1.2.1.4. Thermal isomerization of eight-membered cyclic olefins

Migration of double bonds involving 1,5-hydrogen shifts also takes place (at 225°) in cyclooctatrienes[139,140,141]. In this case, $\Delta E = 3.7$ kcal/mole:

75   76   77
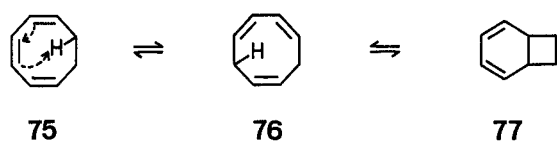
The isomerization of cyclooctadienes at 100 – 130° proceeds via successive 1,5-hydrogen shifts[112]. The reaction 76 → 75 is first order in 76 and is uncatalyzed. Cyclohomotriene, a C_9-ring, also undergoes 1,5-hydrogen shifts; these are, however, due to valence isomerization and are as such not covered by this review.

1.2.1.5. Thermal isomerization of polycyclic unsaturated systems

The thermal isomerizations of palustric and levopimaric (78) acids at 170 and 200° have been studied[142]. Abietic acid (79) is the main product of both isomerizations:

78   79
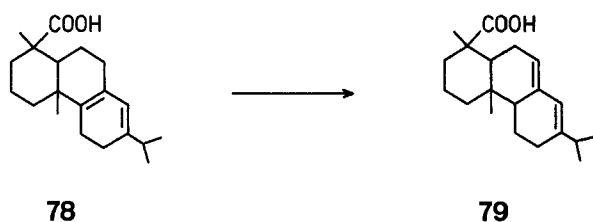
Palustric acid is more thermally stable than levopimaric[142] acid and is less stable than neoabietic acid[143]. It is an intermediate in the thermal (and acid) isomerization of levopimaric acid to abietic acid[143,144]. It appears, however, that the carboxylic acid group in palustric and abietic acid acts as a catalyst in the thermal reaction[144], and therefore the isomerization is rather acid-catalyzed than purely thermal.

Precalciferol (80) is readily isomerized to calciferol (81) by gentle heating[145]:

80   81
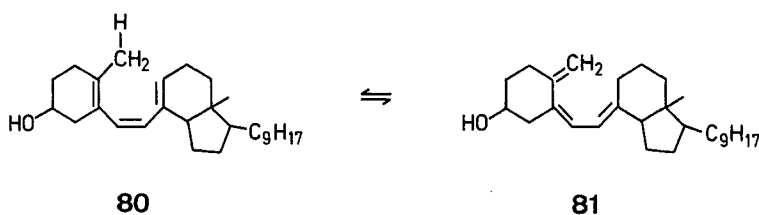
The thermal isomerization of calciferol analogues 82 into the precalciferol analogues 83 also occurs readily and the equilibrium lies far to the "precalciferol" side[111]:

82   83
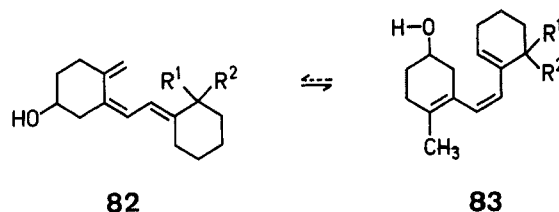
The high negative entropy of activation of the reaction is compatible with a rigid cyclic transition state[111,146], which could explain the 1,7-hydrogen shift which takes place[112].

Thermal isomerization of 2,4-cholestadiene (84) affords 3,5-cholestadiene (89)[147]:

84

85
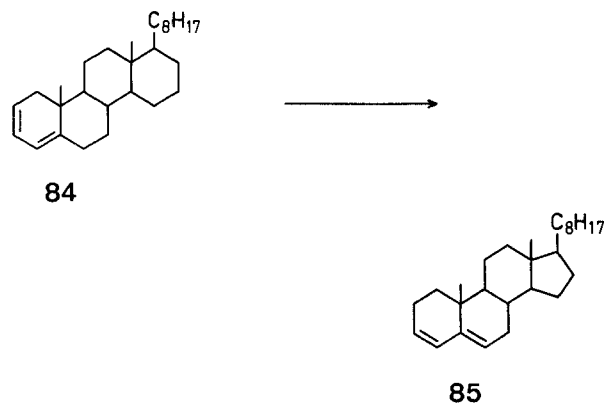
1.2.2. Isomerization of cycloolefins in the presence of catalysts

The isomerization of cyclic olefins in the presence of acids and metal complexes, in solution and on heterogeneous catalysts, has been studied extensively. The same principles active in the case of linear olefins (see Section 1.1.) operate here, but some special factors due to specific conformational effects in the rings also come into play. Thus, a study of the isomerization of a series of methylenecycloalkanes in the presence of p-toluenesulfonic acid in acetic acid[148] revealed that the internal isomers are always

[124] H. Pines, C. T. Chen, J. Amer. Chem. Soc. 81, 928 (1959).
[125] A. P. ter Borg, H. Kloosterziel, N. van Meurs, Proc. Chem. Soc. 1962, 359.
[126] C. Grundmann, G. Ottmann, Liebigs Ann. Chem. 582, 163 (1953).
[127] V. A. Mironov, O. S. Chizhov, I. M. Kimelfeld, A. A. Akhrem, Tetrahedron Letters 1969, 499.

[128] A. P. ter Borg, H. Kloosterziel, Rec. Trav. Chim. 84, 241, 245 (1965).
[129] A. P. ter Borg, H. Kloosterziel, N. van Meurs, Rec. Trav. Chim. 82, 717 (1963).
[130] A. P. ter Borg, H. Kloosterziel, Rec. Trav. Chim. 82, 741 (1963).

more stable than the external isomers. Variations in the stability ratio external isomer: internal isomer depending on the ring size were, however, observed. The values of ΔF^0 for many cycloolefins are in the same order of magnitude as the values of ΔH^0 obtained from heats of hydrogenation[149]. The low stability of methylenecyclohexane as indicated by its ΔH^0 value was rather unexpected and was explained on the basis of an entropy change due to solvation by the acetic acid used in the hydrogenation reaction[148]. In the case of medium-sized rings, the amount of exocyclic isomer present at equilibrium is very small. This is due to the release of ring strain which accompanies the migration of a double bond from the exocyclic to the endocyclic position.

Conformational effects could be clearly observed by studying the migration of double bonds in macrocyclic dienes[150]:

1.2.2.1. Catalytic isomerization of five-membered cycloolefins

1.2.2.1.1. Catalytic isomerization of cyclopentene derivatives

The equilibration of methylcyclopentenes may be achieved on alumina at 200 – 350°; distillation of the resultant mixtures affords the pure isomers[151]. In the equilibrium mixtures obtained from methyl- and ethylcyclopentenes on alumina at 250°, the 1-alkyl isomers are by far the predominant components (80% 1-methylcyclopentene and 71.2% 1-ethylcyclopentene, respectively); the analogous isomerizations of methylcyclohexenes and ethylcyclohexenes give similar results (62.9% 1-methylcyclohexene and 59.8% 1-ethylcyclohexene, respectively)[152,153,154].

The equilibrium between methylenecyclopentane and 1-methylcyclopentene was also studied using p-toluenesulfonic acid in acetic acid as catalyst[146].

Another catalyst employed in the isomerization of methylene- and vinylcyclopentanes is chromium(III)-oxide on alumina (at 250°)[155]. The same catalyst has been used in the isomerization of 3-ethylcyclopentene into the 1-isomer (50% yield)[156]. Allylcyclopentane is isomerized under similar conditions[153] into 1-propylcyclopentene; propenylcyclopentane is an intermediate. Other endocyclic isomers (2- and 3-alkylcyclopentenes) are not formed.

In the cyclopentene series, the endocyclic isomers are most stable, but "contra-thermodynamic" isomerizations can be performed via the organoborane as in the aliphatic series[39].

An interesting "contra-thermodynamic" isomerization, which, however, is of less preparative value than the hydroboration method, is the photoisomerization of 1-methylcyclopentene, 1-methylcyclohexene, and 1-methylcycloheptene in methanol in the presence of benzene, toluene, or xylene as photosensitizers. In the case of 1-methylcyclopentene (which reacts more slowly than its two higher homologs), 24% of methylenecyclopentane is obtained along with the reduction product methylcyclopentane[157], whereas the six- and seven-membered olefins afford mixtures of methylenecyclohexane (-cycloheptane) and 1-methoxy-1-methylcyclohexane (-cycloheptane), respectively[158].

Methylenecyclopentane is isomerized to the endo-isomer under hydroformylation conditions (Co/ ThO$_2$/Kieselguhr + CO + H$_2$)[158]. The isomerization of benzylidenecyclopentane to the less-conjugated 1-benzylcyclopentene under the influence of phosphoric acid has been observed[160].

1.2.2.1.2. Catalytic isomerization of indene derivatives

Both base-catalyzed[1,161] and thermal isomerizations of indene derivatives are known, e. g.

86   **87**
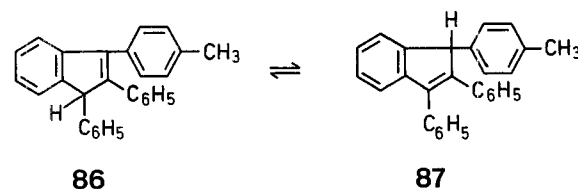
Isomerizations of exocyclic double bonds take place in both indane and indanone derivatives.

[131] A. P. TER BORG, H. KLOOSTERZIEL, Rec. Trav. Chim. 82, 1189 (1963).

[132] K. W. EGGER, J. Amer. Chem. Soc. 89, 3688 (1967).

[133] A. P. TER BORG, E. RAZENBERG, H. KLOOSTERZIEL, Rec. Trav. Chim. 84, 1230 (1965).

[134] A. P. TER BORG, E. RAZENBERG, H. KLOOSTERZIEL, Rec. Trav. Chim. 85, 774 (1966).

[135] E. WETH, A. S. DREIDING, Proc. Chem. Soc. 1964, 59.

[136] T. NOZOE, K. TAKAHASHI, Bull. Chem. Soc. Japan 38, 665 (1965).

[137] A. P. TER BORG, R. VAN HELDEN, A. F. BICKEL, Rec. Trav. Chim. 81, 591 (1962).

[138] A. C. COPE, J. K. HECHT, J. Amer. Chem. Soc. 85, 1780 (1963).

[139] D. S. GLASS, J. ZIRNER, S. WINSTEIN, Proc. Chem. Soc. 1963, 276.

[140] W. R. ROTH, Liebigs Ann. Chem. 671, 25 (1964).

[141] H. KLOOSTERZIEL, A. P. TER BORG, Rec. Trav. Chim. 84, 1305 (1965).

[142] V. M. LOEBLICH, D. E. BALDWIN, R. T. O'CONNOR, R. V. LAWRENCE, J. Amer. Chem. Soc. 77, 6311 (1955).

[143] V. M. LOEBLICH, D. E. BALDWIN, R. V. LAWRENCE, J. Amer. Chem. Soc. 77, 2823 (1955).

[144] L. RUZICKA, F. BALAS, F. VILIM, Helv. Chim. Acta 7, 458 (1924).

[145] L. VELLUZ, G. AMIARD, B. GOFFINET, Bull. Soc. Chim. France 1955, 1341.

[146] M. LEGRAND, J. MATHIEU, C. r. Acad. Sci. Paris 245, 2502 (1957).

[147] H. E. STAVELY, W. BERGMANN, J. Org. Chem. 1, 567 (1936).

[148] A. C. COPE et al., J. Amer. Chem. Soc. 82, 1750 (1960).

[149] R. B. TURNER, R. H. GARNER, J. Amer. Chem. Soc. 80, 1424 (1958).

Acid-catalyzed isomerizations of indenes have only recently been observed[162]. It was found that equilibria between alkylindenes (88) and alkylidene indanes (89) exist at 80° in the presence of sulfuric acid or *p*-toluenesulfonic acid/alcohol:
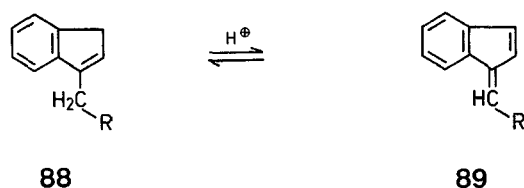
The position of the equilibrium is dependent on the nature of group R; if R = aryl or (especially) methyl, 88 predominates at equilibrium, but if R = aroyl, 55–60% of 89 is found in the reaction mixture. Electron-donating groups such as a methyl group in the *p*-position of the phenyl substituent slightly favor isomer 89; ortho-substituents decrease the amount of 89 in the reaction mixture.

The fact that 3-benzylindene (88) is more stable than benzylideneindane (89) is demonstrated by the enthalpy difference in favor of 89 of $\Delta H \sim 0.8$ kcal/mol. This stability difference is probably due to the fact that in 89 two CH_2-groups are kept rigidly in an eclipsed conformation. Such a conformation should increase the internal energy of 89 relative to 88 by about 3 kcal/mol. Since there is a difference in the resonance energies between 88 and 89 of ~ 2 kcal/mol, leading to an expected enthalpy difference in favor of 88 of ~ 1 kcal/mol, the determined ΔH above lies in the expected order of magnitude.

The equilibrium reaction doubtless proceeds through the tertiary cation 90.
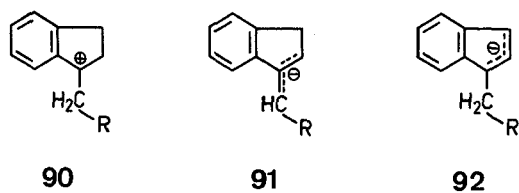
This might explain why base-catalyzed isomerizations of alkylindenes do not generally give the exocyclic isomer: the formation of anion 91 proceeds less readily than that of 92. The isomerization of 1-alkylindenes to the 3-isomer in the presence of base takes place through anion 92, and occurs readily. Formation of 89 via anion 91 in the equilibrium 88 ⇌ 89, however, only takes place under drastic conditions[162].

The physical properties and equilibrium compositions of various *exo-endo*-isomer pairs 88 and 89 are summarized in Table 1.

Table 1. Physical Properties of Isomer Pairs 88 and 89[163]

Composition of the Mixture 88–89 at Equilibrium, $T \sim 90°$ Catalyst: H_2SO_4 (1%). Reaction time = 24 hours. Solvent: Ethanol 80%; Water 20%.

R	m. p. 88	m. p. 89	% (89)* at Equilibrium
	liquid	75°	33 (33)
CH₃	liquid	–	18.5
-CH₃	liquid	83°	39 (43)
OCH₃	liquid	–	23
-OCH₃	92°	96°	39 (39.5)
-Cl	liquid	–	34.4
	58°	–	44
-CH₃	liquid	liquid	3 (3)

* The values in brackets are those obtained by isomerization of 89 into 88; otherwise, the starting material was 88.

The acid-catalyzed isomerization of benzylindenes to benzylidene indanes represents a convenient method for the preparation of the latter difficulty accessible compounds[162]. However, it is apparent that the benzylidene indane (89, $R = C_6H_5$) obtained[164] by dehydration of 1-hydroxy-1-benzylindane
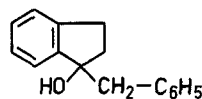
was a mixture of compounds 88 and 89 ($R = C_6H_5$).

[150] A. J. Hubert, J. Dale, J. Chem. Soc. 1963, 4091.

[151] U.S. Patent 2485964 (1949), G. M. Good, H. H. Voge (Shell Development Co.); C. A. 44, 3017 (1950).

[152] E. Gil-Av, J. Shabtai, Chem. & Ind. 1959, 1630.

[153] J. Herling, J. Shabtai, E. Gil-Av, J. Amer. Chem. Soc. 87, 4107 (1965).

[154] See the analogous base-catalyzed isomerizations [Part 1 of this review, Synthesis 1969, 106] and the predictions made by Brown et al. [H. C. Brown, J. H. Brewster, H. Shechter, J. Amer. Chem. Soc. 76, 467 (1954)] concerning the relative stabilities of exo- and endocyclic olefins in the five- and six-membered series.

[155] R. Y. Levina, N. N. Mezentsova, P. A. Akishin, Zh. Obshch. Khim. 23, 562 (1953); C. A. 48, 6970 (1954).

[156] R. Y. Levina, N. N. Mezentsova, P. A. Akishin, Vestnik Moskov Univ. 7, No. 2, Ser. Fiz. Mat. i Estestven. Nauk No. 1, 87 (1952); C. A. 47, 3248 (1953).

[157] P. J. Kropp, J. Amer. Chem. Soc. 89, 3650 (1967).

[158] P. J. Kropp, H. J. Krauss, J. Amer. Chem. Soc. 89, 5199 (1967).

[159] B. K. Nefedov, Y. T. Eidus, Izv. Akad. Nauk SSSR, Ser. Khim. 1966, 533; C. A. 65, 5378 (1966).

On the other hand, benzylidene indane may only be obtained in very low yield by reaction of indene with sodium benzylate $(0.8\%)^{165}$ or by a Wittig reaction[166] (9%). Using the isomerization procedure[162], however, the desired **89** (R = C_6H_5) can readily be separated from benzylindene; the latter compound can be recyclized.

Addition of hydrochloric acid to a solution of **93** in methanol affords[167] 1-(4-methoxybenzylidene)-indane (**89**, R = 4-methoxyphenyl), which precipitates directly from the reaction mixture. The low solubility of the product in methanol prevents its isomerization; however, if an ethanolic solution of this material is allowed to reflux, the expected equilibration takes place[162]. Analogously, treatment of **95** with hydrochloric acid gives **96**; isomerization of the latter to **97** is observed after one hour under the same reaction conditions[167]:

93   **94**

95   **96**

97
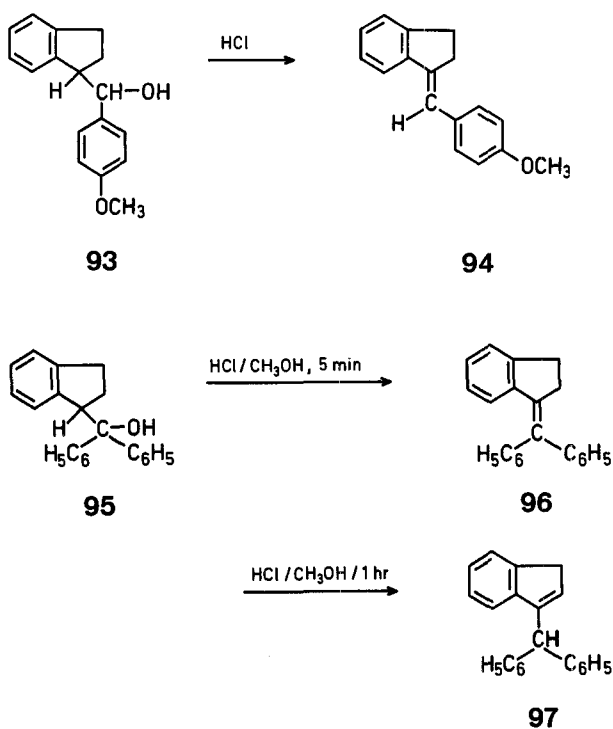
It is of interest that **99** cannot be prepared by dehydration of **98**; **100** is isolated instead[168]. The possibility that an equilibrium between the two isomers exists has not yet been investigated:

98   **99**

100
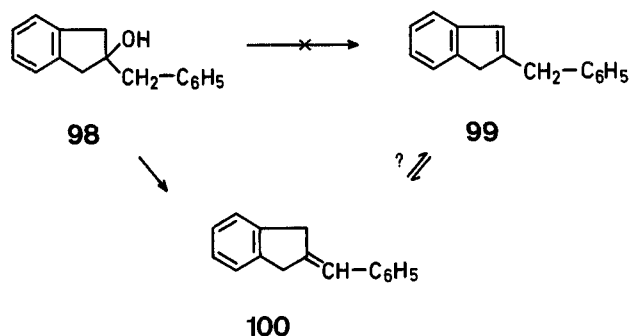
Isomerization of 1-methylindene (**101**) into the 3-isomer **102** does not occur with acid catalysts, but the use of palladium on charcoal readily induces this bond migration[169]:

101   **102**

The isomerization of cycloheptatrienylindene into benzylidene indane (see Part I, p. 104) is catalyzed by hydrochloric acid as well as by bases.

Methylenebicycloheptane (**103**) is readily isomerized to **104** at 250° in the presence of silicophosphoric acid[170]. The reverse reaction can also be made to take place, but is accompanied by skeletal rearrangement:

103   **104**

The isomerization of **105** into **106** in the presence of trifluoroacetic acid involves an intramolecular 1,3-hydrogen shift[171]:

105   **106**
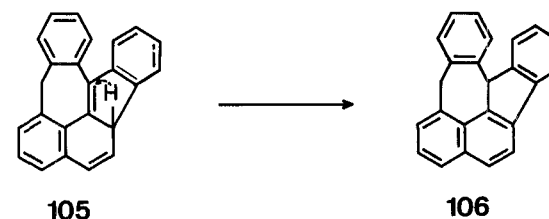
[160] H. J. SCHAEFFER, C. J. COLLINS, J. Amer. Chem. Soc. **78**, 124 (1956).
[161] C. F. KOELSCH, J. Amer. Chem. Soc. **56**, 1337 (1934).
[162] A. J. HUBERT, H. REIMLINGER, J. Chem. Soc. [C] **1969**, 944.
[163] A. J. HUBERT, H. REIMLINGER, unpublished results.
[164] A. A. PLENTL, M. T. BOGERT, J. Amer. Chem. Soc. **63**, 989 (1941).
[165] S. S. HIRSCH, D. H. LORENZ, E. I. BECKER, J. Org. Chem. **23**, 1829 (1958).
[166] G. WITSCHARD, C. E. GRIFFIN, J. Org. Chem. **29**, 2335 (1964).
[167] C. COURTOT, Ann. Chim. [9] **5**, 52 (1916).
[168] N. CAMPBELL, H. G. HELLER, J. Chem. Soc. **1962**, 3006.
[169] H. CHRISTOL, F. PLENAT, C. F. HUEBNER, Bull. Soc. Chim. France **1964**, 2640.
[170] M. BLANCHARD, J. E. GERMAIN, C. r. Acad. Sci. Paris **254**, 3351 (1962).
[171] P. T. LANSBURY, K. R. FOUNTAIN, J. Amer. Chem. Soc. **90**, 6544 (1968).
[172] A. A. KUBASOV, E. V. SMIRNOVA, K. V. TOPCHIEVA, Kinetica i Kataliz **8**, 146 (1967); C. A. **67**, 21468 (1967).

[173] J. CHAMPAGNE, H. FAVRE, D. VOCELLE, I. ZBIKOWSKI, Canad. J. Chem. **42**, 212 (1964).
[174] R. A. BENKESER, J. J. HAZDRA, J. Amer. Chem. Soc. **81**, 228 (1959).
[175] O. WALLACH, Liebigs Ann. Chem. **360**, 26 (1908).
[176] J. W. WILT, D. D. ROBERTS, J. Org. Chem. **27**, 3434 (1962).
[177] H. CHRISTOL, R. VANEL, Bull. Soc. Chim. France **1968**, 1398.
[178] J. W. POWELL, M. C. WHITING, Proc. Chem. Soc. **1960**, 412.

1.2.2.2. Catalytic isomerization of six-membered cycloolefins

Cyclohexenes are isomerized under the same conditions as the cyclopentene derivatives. For example, 1-alkylcyclohexenes are isomerized into 1-alkyl-2-cyclohexenes in the presence of chromium(III)-oxide/alumina[155]. At 220° in the presence of alumina, 1-methyl-1-cyclohexene isomerizes to 1-methyl-3-cyclohexene[172]. Equilibration of 4,4-dimethylcyclohexene (107) and its 3,3-isomer (108) occurs in the presence of p-toluenesulfonic acid[173]. In this case, 107 is the more stable isomer ($\Delta F = 0.73 - 0.78$ kcal/mol).

107 108

Phenylcyclohexene (109) undergoes ring contraction when heated with 85% phosphoric acid at reflux temperature; however, under the same conditions, the isomerization of 109 into 110 has been observed[118,119]:

109 110
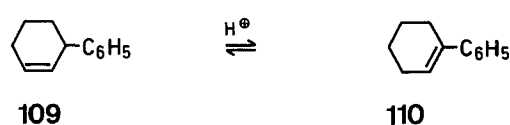
The isomerization of alkylidenecyclohexanes to their *endo*-isomers proceeds readily in the presence of an acidic catalyst such as p-toluenesulfonic acid[148,174]. The isomerization of methylenecyclohexane into 1-methylcyclohexene in the presence of acids was described more than 50 years ago[175].

Acids may also be used[176] to equilibrate 1-benzyl-1-cyclohexene (111) and its exocyclic isomer 112:

111 112
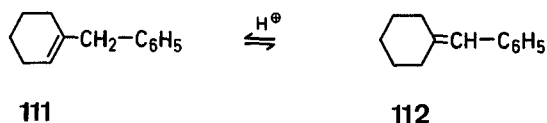
The isomerization of spiro compound 113 to 114 takes place using potassium hydrogen sulfate as catalyst[177]:

113 114
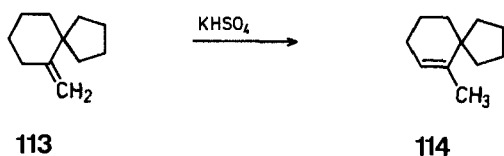
Similarly, various catalysts have been used to isomerize $\Delta^{1,9}$-octalin and *trans*-Δ^1-octalin[178]. The latter gives rise[178] to a mixture of Δ^9-octalin and $\Delta^{1,9}$-octalin, together with four other isomers, in a ratio of about 90:9:1. The reagent tetrafluoroboric acid in benzene/tetrahydrothiophene-1,1-dioxide was found to be a particularly efficient catalyst for this isomerization.

Isomerizations of various polyenes of the vitamin A type have been studied; hydrogen bromide, alumina, and bases are reported to be effective catalysts[179].

115

116
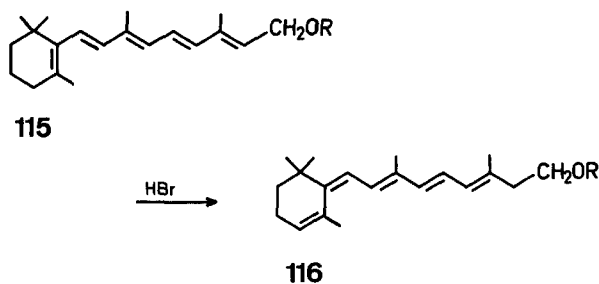
The photoisomerization of alkylcyclohexenes in aromatic solvents leads to the corresponding exocyclic isomers; the aromatic hydrocarbon serves as photosensitizer. Thus, 117 is isomerized to 118[180,181] and 119 to 120[180]:

117 118

119 120
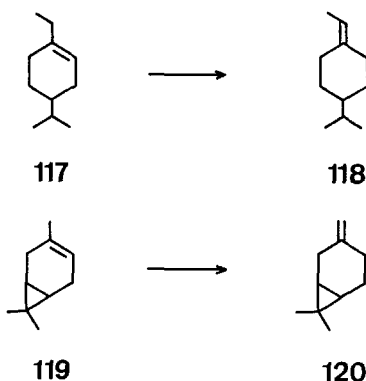
[183] E. H. FARMER, C. G. MOORE, J. Chem. Soc. 1951, 149.

[184] R. Y. LEVINA, F. F. TZURIKOV, Zh. Obshch. Khim. 4, 1250 (1934); C. A. 29, 3314 (1934).

[185] A. I. PERELMAN, E. A. MUSHINA, A. V. TOPCHIEV, Plasticheskie Massy 1964, 3; C. A. 61, 16163 (1964).

[186] Y. M. SLOBODIN, Zh. Obshch. Khim. 6, 129 (1936); C. A. 30, 4828 (1936).

[187] R. Y. LEVINA, N. N. MEZENTSOVA, P. A. AKISHIN, Vestnik Moskov Univ. 6, no. 2, Ser. Fiz. Mat. i Etestven. Nauk no. 1, 77 (1951); C. A. 46, 8620 (1952).

[188] R. Y. LEVINA, N. N. MEZENTSOVA, P. A. AKISHIN, Vestnik Moskov Univ. 7, no. 12, Ser. Fiz. Mat. i Etestven, no. 8, 49 (1952); C. A. 48, 4455 (1954).

[189] J. CHAMPAGNE, H. FAVRE, D. VOCELLE, I. ZBIKOVZKI, Canad. J. Chem. 42, 212 (1964).

[190] R. L. FRANK, R. E. BERRY, J. Amer. Chem. Soc. 72, 2985 (1950).

[191] A. A. PETROV, N. P. SOPOV, Doklady Akad. Nauk SSSR, 79, 811 (1950); C. A. 46, 7064 (1952).

[192] K. H. BELL, Chem. Commun. 1967, 397.

[193] H. CHRISTOL, F. PLENAT, Bull. Soc. Chim. France 1962, 1325.

[194] F. SONDHEIMER, R. MECHOULAM, J. Amer. Chem. Soc. 79, 5029 (1957).

[179] K. MACKENZIE, in: S. PATAI, The Chemistry of Alkenes, Interscience Publishers, London·New York·Sidney, 1964, p. 434.

[180] P. J. KROPP, J. Amer. Chem. Soc. 88, 4091 (1966).

[181] J. A. MARSHALL, R. D. CARROLL, J. Amer. Chem. Soc. 88, 4092 (1966).

[182] J. A. MARSHALL, A. R. HOCHSTETLER, J. Amer. Chem. Soc. 91, 648 (1969).

However, in aromatic solvents the isomerization of the olefin is accompanied by substantial dimerization. Especially in the case of cyclohexenes, better results may be obtained by carrying out the isomerization reaction in protic media such as alcohols in the presence of a small amount of xylene as photosensitizer. The formation of tertiary ethers as by-products in these reactions, e. g., in the isomerization of 1-methylcyclohexene (121, R = H) to methylenecyclohexane (122, R = H) in methanol (R' = CH₃) in the presence of xylene,

121   **122**
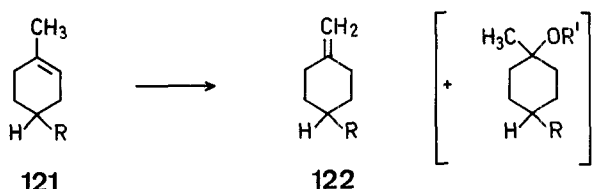
can be satisfactorily eliminated by using isopropanol or *t*-butanol as protic solvent. Thus, U.V.-irradiation of the octalin 123 in isopropanol in the presence of xylene affords[182] the methylenedecalin 124:

123   **124**
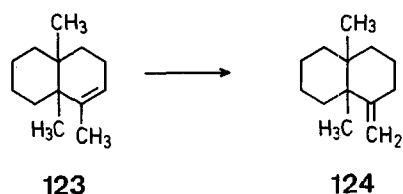
In contrast to the isomerization in aromatic hydrocarbon solvents, an ionic mechanism is operative[159] when alcohols are used as solvents.

Cyclohexenes may be isomerized in the presence of radicals. Thus, reaction of methylcyclohexene with hydroxyl radicals induces the double bond migration indicated[183]:


Metallic catalysts have also been used to isomerize cyclohexenes. For example, methylenecyclohexane is isomerized in the presence of palladium into its internal isomer[184].

Vinylcyclohexane (125) gives ethylidenecyclohexane (126) when titanium(IV)-chloride/triisobutylaluminum is used as catalyst[185].

125   **126**
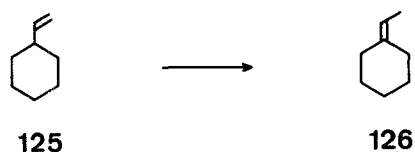
In the presence of floridin (Fuller's earth), 4-vinylcyclohexene (127) isomerizes at 210–240° to 3-ethylidenecyclohexene (128)[186]; under the same conditions, limonene (129) gives 130:

127   **128**

129   **130**
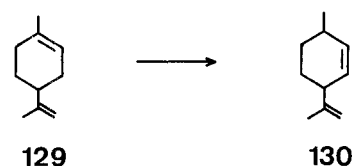
Vinyl- and allyl cyclohexanes are transformed at 250° into 1-ethylcyclohexene and 1-propylcyclohexene, respectively, employing chromium(III)-oxide on alumina as catalyst[187]. Using the same catalyst, equilibration of 1-ethylcyclohexene takes place to produce 15% of 3-ethylcyclohexene and of 3-ethylcyclohexene to give 50% of 1-ethylcyclohexene[157]. Similarly, methylenecyclohexane is isomerized at 250° on chromium(III)-oxide-on-alumina to give a mixture containing 60% of 1-methylcyclohexene, 33% of the 3-isomer, and traces of 4-methylcyclohexene[188].

In the equilibration mixture obtained on prolonged treatment of either 131 or 132 with *p*-toluenesulfonic acid in boiling acetic acid, 4,4-dimethylcyclohexene (132) predominates[189]:

131 (30 %)   **132** (70 %)
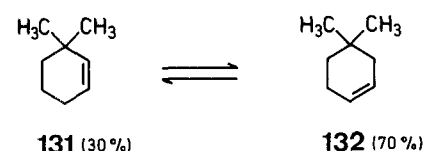
[195] J. B. Bream, D. C. Eaton, H. B. Henbest, J. Chem. Soc. 1957, 1974.

[196] G. Brownlie, M. B. E. Fayez, F. S. Spring, R. Stevenson, W. S. Strachan, J. Chem. Soc. 1956, 1377.

[197] E. I. Prokopets, G. E. Gavrilova, L. A. Klimova, J. Applied Chem. (USSR), 11, 850 (1938); C. A. 33, 1717 (1939).

[198] U.S. Patent 3359342 (1967), J. M. Derfer (Glidden Co.); C. A. 68, 49816 (1968).

[199] H. C. Brown, M. V. Bhatt, T. Munekata, G. Zweifel, J. Amer. Chem. Soc. 89, 567 (1967).

[200] R. B. Turner, W. R. Meador, R. E. Winkler, J. Amer. Chem. Soc. 79, 4122 (1957).

[201] U.S. Patent 2838527 (1958), G. Lauback, K. J. Brunnings, (Chas. Pfizer & Co.); C. A. 52, 18533 (1958).

[202] R. Borsdorf, B. Olesch, J. prakt. Chem. [4] 36, 165 (1967).

[203] K. Conrow, L. L. Reasor, J. Org. Chem. 30, 4368 (1965).

[204] K. Conrow, J. Amer. Chem. Soc. 83, 2343 (1961).

[205] R. E. Rinehart, J. S. Lasky, J. Amer. Chem. Soc. 86, 2516 (1964).

[206] J. K. Nicholson, B. L. Shaw, Tetrahedron Letters 1965, 3533.

[207] H. Frye, E. Kuljian, J. Viebrock, Inorg. Chem. 4, 1499 (1965).

[208] German Patent 1136329 (1962), P. Wittenberg, H. Seibt (BASF): C. A. 58, 4442 (1963).
see also: K. N. Anisimov, A. A. Ioganson, N. E. Kolobova, Uspechi Khimii 1968, 380; Russian Chem. Reviews 1968, 184.

The isomerization of **133**, which is very stable under alkaline conditions, into **134** and **135** takes place on alumina at 400°, in the presence of sulfuric acid in aqueous ethanol, or using hydrogen chloride in acetic acid as catalyst[190]. A number of other products are also present in the mixture obtained:


133   **134**   **135**
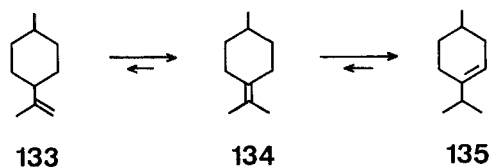
Hydrochloric acid catalyzes[191] the isomerization of **136** to **137**.

**136**   **137**
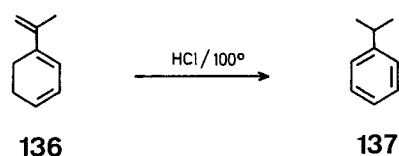
Isomerization of **138** to **139** takes place in the presence of hydrogen chloride or boron trifluoride[192]; the double bond migration is followed by a methyl group shift giving rise to **140**:

138

139   **140**
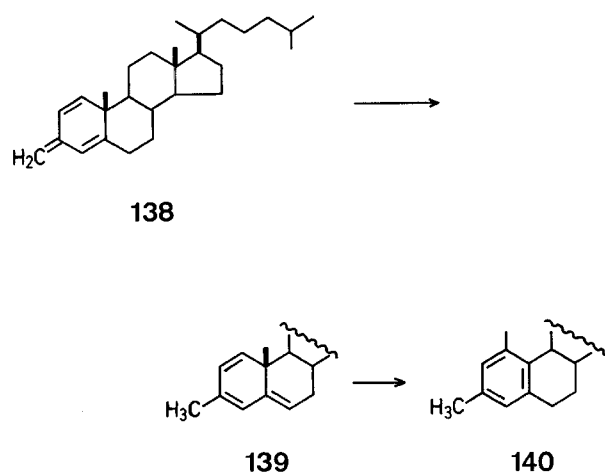
The exocyclic olefin **141** is readily isomerized to **142** in the presence of p-toluenesulfonic acid[193]:

**141**   **142**
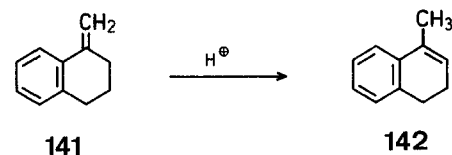
The isomerizations of 3-methylene-Δ^4-cholestene (**143**, R=C_8H_{17}) and 17β-hydroxy-3Δ^4-androstene (**143**, R=OH) demonstrate the usefulness of double bond shifts in the synthesis of natural products and their derivatives[194].

143

144
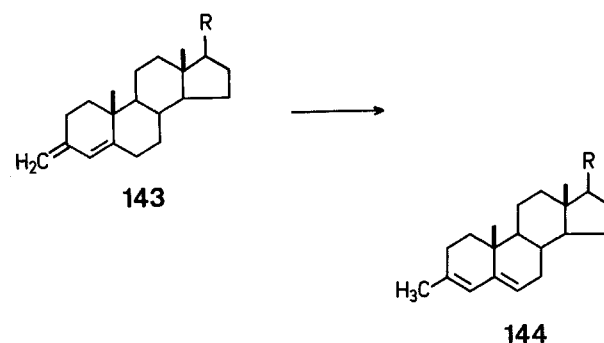
Migration of double bonds in steroids in the presence of hydrogenation catalysts (e.g. palladium)[195] have also been observed[195].

Treatment of either Δ^{18}-oleanene (**145**), Δ^{12}-oleanene (**146**), or Δ^{12}-18α-oleanene (**147**) with hydrochloric acid[196] gives rise to an equilibrium mixture of **147** and **148**:

147

145   **148**

146
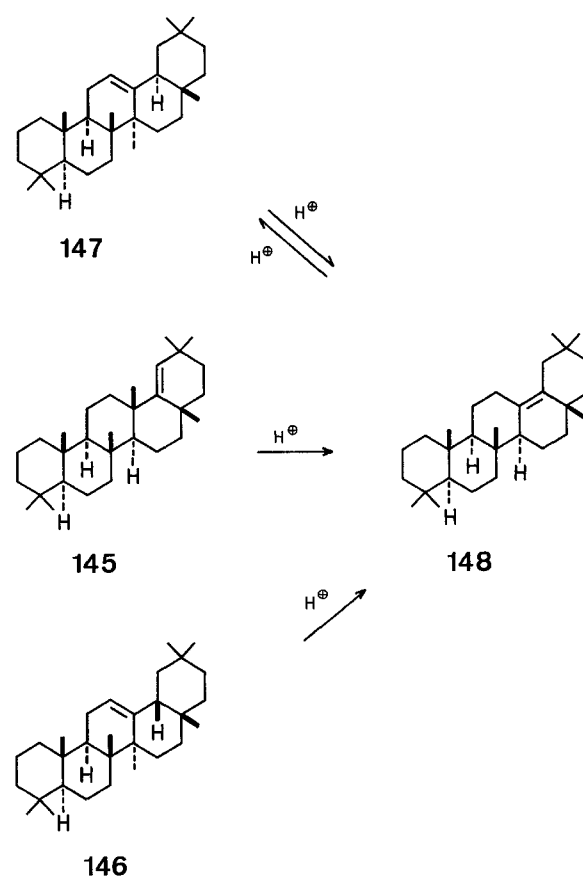
[209] J. E. ARNET, R. PETTIT, J. Amer. Chem. Soc. **83**, 2954 (1961).

[210] H. MASAI, K. SONOGASHIRA, N. HAGIHARA, Mem. Inst. Sci. Ind. Res. Osaka Univ. **25**, 117 (1968); C. A. **69**, 66 948 (1968).

[211] K. M. SHUMATE, G. J. FONKEN, J. Amer. Chem. Soc. **88**, 1073 (1966).

[212] J. G. TTAYNHAM, W. C. BAIRD, J. Org. Chem. **27**, 3189 (1962).

[213] P. HEIMBACH, Angew. Chem. **78**, 604 (1966); Angew. Chem., Intern. Edit. **5**, 595 (1966).

[214] A. J. HUBERT, J. DALE, J. Chem. Soc. **1963**, 4091.

[215] J. C. COWAN, J. Amer. Oil Chemists' Soc. **27**, 492 (1950).

[216] J. BALTES, Fette und Seifen **52**, 462 (1950).

[217] Y. WATANABE, Bull. Chem. Soc. Japan **33**, 1319 (1960); C. A. **55**, 14 293 (1961).

[218] V. S. VARLAMOV, Trudy Vsesoyuz. Nauch.-Issledovatel. Inst. Zhirov. **1958**, 114; C. A. **55**, 21 623 (1961).

[219] J. J. A. BLEKKINGH, H. J. J. JANSSEN, J. G. KEPPLER, Rec. Trav. Chim. **76**, 35 (1957).

[220] Y. TSUCHIYA, M. KAYAMA, Tohoku, J. Agr. Research **7**, 277 (1957); C. A. **52**, 2428 (1958).

A molybdenum sulfide catalyst (MoS_2) has been used for the isomerization of symmetrical octahydroanthracene into its unsymmetrical isomer[197].

Group VIII metal catalysts[198] such as palladium on alumina and Raney nickel may be used for the partial isomerization (up to 7%)[197] of α-pinene into β-pinene in the gas phase at 170–200°. "Contrathermodynamic" isomerization of methylcyclohexene to methylenecyclohexane (and of α-pinene to β-pinene) can be achieved using the general method of hydroboration[199].

Cyclohexadiene may be isomerized at 125° using a catalyst consisting of a mixture of an iron salt (e.g., iron ethylhexanoate) and an organoaluminum compound (e.g., triethylaluminum)[93].

$\varDelta^5$-Cholestene is equilibrated at 85° by p-toluenesulfonic acid/acetic acid in cyclohexane to form a mixture of $\varDelta^5$-cholestene (45%) and $\varDelta^4$-cholestene (55%)[200]. The difference of enthalpy between the isomers is 0.1 kcal/mol.

Isomerization of $\varDelta^{6,8(14),9(11)}$-steroidal trienes takes place at 100° in the presence of sulfur dioxide in benzene containing hydroquinone and pyridine[201].

1.2.2.3. Catalytic isomerization of seven- and eight-membered cycloolefins

The uncatalyzed thermal isomerizations of this series have been extensively studied. In addition, it has been shown that 1-methylcycloheptene is isomerized by light in a solution of an alcohol into methylenecycloheptane[203]. Treatment of methylenecycloheptane with p-toluenesulfonic acid in acetic acid at 25° gives 1-methylcycloheptene (98.7%)[148]. An equilibrium between some other 1-alkylcycloheptenes and their exo-isomers has been observed[201]; the concentration of the exo-isomer at equilibrium varies from 1% (alkyl = CH_3) to 30% (alkyl = C_2H_5, i-C_3H_7).

Isomerization of 7-methyltropilidene (149) may be carried out in the presence of acidic catalysts such as phosphoric acid and picric acid[203]. The composition of the isomerized mixture varies with the catalyst; the distribution obtained using phosphoric acid is similar to that of the equilibrium mixture,

149
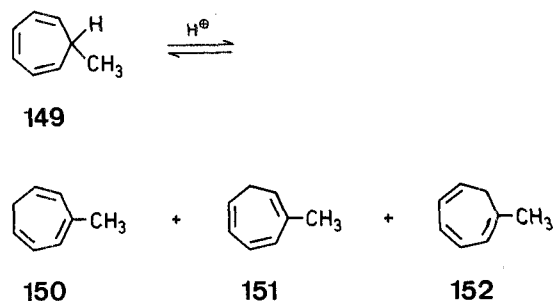
150   **151**   **152**

which has been determined using tropylium perchlorate as catalyst[204]:

Isomer	149 150 151 152
Ratio	4.6 : 16.1 : 9.6 : 69.7

The isomerization of methylenebenzocycloheptene (153) to its internal isomer (154) was effected at 50° in the presence of p-toluenesulfonic acid:


153   **154**
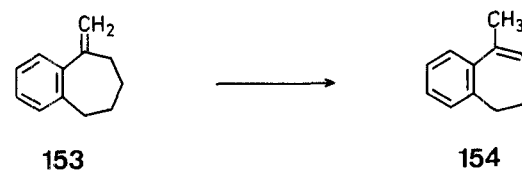
The next higher homolog (methylenebenzocyclooctene) is, however, not isomerized under the same conditions[190].

The most striking feature of the isomerization in the cyclooctadiene series is the "deconjugation" of the double bonds in the presence of complex metal catalysts (e.g., rhodium)[205,206]. The reaction is not,

[221] Japanese Patent 8056/55, K. Tanabe (Agency of Industrial Science and Technology); C. A. **51**, 18645 (1957).

[222] S. B. Radlove et al., Ind. Eng. Chem. **38**, 977 (1946).

[223] F. Battline, Paint, Oil Chem. Rev. **105**, 13 (1943).

[224] S. B. Radlove, H. M. Teeter, J. C. Cowan, U.S. Dept. Agr., Bur. Agr. Ind. Chem. AIC **101**, 1 (1945); C. A. **41**, 1472 (1947).

[225] H. I. Waterman, C. van Vlodrop, Rec. Trav. Chim. **57**, 629 (1938).

[226] R. Rigamonti, F. Grosa, Olearia **7**, 183 (1953); C. A. **48**, 12428 (1954).

[227] U.S. Patent 3278567 (1966), W. E. Rathjen, L. O. Cummings, J. A. Kneeland, (Pacific Vegetable Oil Corp.); C. A. **66**, 11926 (1967).

[228] J. H. de Boer, J. P. W. Houtman, H. I. Waterman, Koninkl. Nederland Akad. Wetenschap., Proc. **50**, 1181 (1947).

[229] H. I. Waterman, J. van Steenis, J. H. de Boer, Research (London) **2**, 583 (1949); C. A. **44**, 3883 (1950).

[230] K. H. Takemura, L. A. Goldblatt, J. Amer. Oil Chemists' Soc. **34**, 15 (1957).

[231] A. L. Markman, V. N. Rozhkova, Uzb. Khim. Zh. **10**, 11 (1966); C. A. **66**, 86868 (1967).

[232] J. C. Bailar, H. Itatani, M. J. Crespi, J. Geldar, Adv. Chem. Ser. **62**, 103 (1967).

[233] German Patent 1267682 (1968), H. Müller, H. Koehl, H. Pommer (BASF); C. A. **69**, 7152 (1968).

[234] A. Turk, P. D. Moore, Oil and Soap **21**, 321 (1944).

[235] A. A. Ivanova, A. S. Petrova, Khim. Prom. **1947**, 20; C. A. **43**, 4027 (1949).

[236] T. Hashimoto, H. Shiina, Tokyo Kogyo Shikensho Hokoku **61**, 261 (1966); C. A. **65**, 18876 (1966).

[237] R. Damico, J. Org. Chem. **33**, 1550 (1968).

[238] G. Riezebos, A. G. Peto, B. North, Rec. Trav. Chim. **86**, 31 (1967).

[239] U.S. Patent 2575529 (1951), S. B. Radlove (Maytag Co.); C. A. **46**, 4812 (1952).

[240] O. Prakash, A. Ram, V. D. Athawale, S. C. Pandey, Paintindia **5**, 21 (1956); C. A. **50** 14241 (1956).

[241] W. Treibs, Fette und Seifen **52**, 549 (1950).

[242] G. Scott, Atmospheric Oxidation and Antioxidants, Elsevier Publishing Co., Amsterdam·New York·London, 1965.

however, catalytic, but proceeds through a complex in which the two double bonds assume the 1,5 position with respect to one another. The cyclo-olefin is liberated from the complex by treatment with cyanide ion[205,206]:

155

156
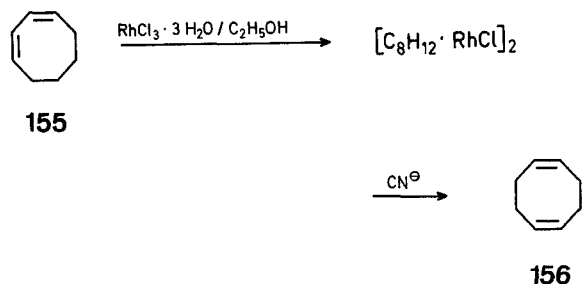
The complexes of palladium and platinum have also been used in this isomerization[207]:

$C_8H_{12} \cdot MX_2$ (M = Pd, Pt; X = Cl, Br)
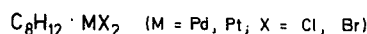
In these cases, the 1,5-diene is also liberated from the complex using cyanide anion. The "normal" isomerization in the cyclooctadiene series, i.e., the conversion of 1,5-cyclooctadiene (156) into the thermodynamically more stable 1,3-isomer (155), can be achieved by employing catalysts such as dekacarbonyl-dimanganese[208] [$Mn_2(CO)_{10}$], penta-carbonyliron[209] [$Fe(CO)_5$], or π-cyclopentadienyl-titanum derivatives[210].

Methylenecyclooctane is quantitatively isomerized in acetic acid in the presence of p-toluenesulfonic acid at 25° to give 1-methylcyclooctene[148].

1.2.2.4. Catalytic isomerization of unsaturated medium-sized rings and macrocyclic olefins

Methylenecyclononane is quantitatively isomerized into its *endo*-isomers using p-toluenesulfonic acid in acetic acid[148] at 25°. Irradiation of *cis, trans*-1,3-cyclononadiene with U.V. light gives the *cis, cis*-isomer; this is further isomerized under the reaction conditions to a mixture of bicyclic olefins and *cis, cis*-1,4-cyclononadiene[211].

Methylenecyclodecane has been isomerized into its endocyclic isomers using p-toluenesulfonic acid in acetic acid[148] at 25° and hydrobromic acid in acetic acid[212].

U.V.-irradiation of *cis, trans*-1,5-cyclodecadiene in the presence of pentacarbonyliron affords *cis,cis*-1,6-cyclodecadiene[213].

Macrocyclic (C_{12}—C_{22}) alkadienes may be isomerized by heating them in the presence of triethyl-borane[214]. The equilibrium isomer distribution is reached at 200°. The relative distribution of the conjugated and non-conjugated double bond isomers in the product depends strongly on the size of the ring. In cases of rings larger than C_{13}, the conjugated isomer is most stable.

The distribution of the non-conjugated isomers at equilibrium depends on conformational effects: in the case of the 14-, 18-, and 22-membered rings, the symmetrical diene is preferred, whereas asymmetrical isomers are favored in the case of C_{12}-, C_{16}-, and C_{20}-membered rings. The explanation for this phenomenon has been discussed in Part I.

## 2. Isomerization of Olefins containing Hetero Atoms

2.1. Isomerization of Olefins containing Carbonyl Functions

As already noted in Part I.[1], the isomerization of unsaturated acids and natural oils to the corresponding conjugated isomers has been extensively studied in connection with the modification of the properties of drying oils and as an analytical means to measure the unsaturation in such oils.

In general, basic catalysts are used. There are, however, many literature reports on the use of acidic isomerization catalysts, particularly in connection with drying oils[215,216]. The same types of acidic catalysts as described for olefinic hydrocarbons are used with unsaturated fatty acids. Some commonly used acids are: sulfuric acid, phosphoric acid, acetic acid[214], and phosphotungstic acid $(2 H_3PO_4 \cdot WO_3)^{218}$.

Nickel catalysts, sulfur dioxide, and iodo compounds are even more versatile isomerization catalysts[215]. Particularly the nickel catalysts, generally used on an active carbon support, have found a broad application[215,216,218–226].

The isomerization with sulfur dioxide as catalyst[215,227,228] proceeds *via* addition of sulfur dioxide, subsequent rearrangement, and finally elimination of the SO_2 moiety[228]. Unsaturated acids such as 157 are isomerized to the 2-isomers (e.g., 158)[229]:

$$H_2C=CH-CH_2-COOH \xrightarrow{\ SO_2\ } H_3C-CH=CH-COOH$$

       157   **158**
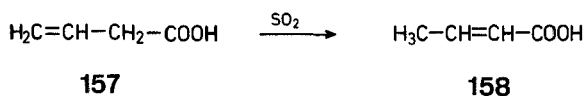
[243] U.S. Patent 2558902 (1952), L. P. WIEBE (Shell Development Co.); C. A. **46**, 6855 (1952).

[244] S. UENO, H. SAKURAI, Kogyo Kagaku Zassi (J. Chem. Soc. Japan, Ind. Chem. Sect.) **52**, 256 (1949); C. A. **45**, 4463 (1951).

[245] R. C. FUSON, J. A. HAEFNER, J. Org. Chem. **27**, 1957 (1962). c.f. Part I of this review.

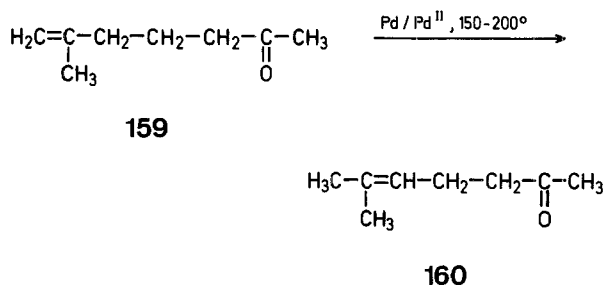[246] K. J. CROWLEY, R. A. SCHNEIDER, J. MEINWALD, J. Chem. Soc. [C] **1966**, 571.

[247] H. J. KROPP, H. J. KRAUSS, J. Org. Chem. **32**, 3222 (1967).

[248] N. HEAP, G. H. WHITHAM, J. Chem. Soc. [B] **1966**, 164.

[249] I. N. NAZAROV, A. N. ELIZAROVA, Izv. Akad. Nauk SSSR, Ser. Khim. **1951**, 295; C. A. **46**, 914 (1952).

[250] R. B. MORIN, D. O. SPRY, K. L. HAUSER, R. A. MUELLER, Tetrahedron Letters **1968**, 6026.

Palladium and platinum catalysts have also been employed to induce double bond isomerization in natural oils. These metals have been used on an active carbon support[230], without support (during hydrogenation)[231], and as complexes such as $(R_3Q)_2NiX_2$ [R = alkyl, aryl, phenoxy; Q = P, As, Sb; X = halogen] and $(R_3Q)_2M(SnX_3)X$ [M = Pd, Pt][232]. A mixture of elemental palladium and palladium(II) compounds[233] has been used to isomerize **159** to **160**:

$$H_2C=\underset{\underset{CH_3}{|}}{C}-CH_2-CH_2-CH_2-\underset{\underset{O}{\|}}{C}-CH_3 \quad \xrightarrow{Pd\,/\,Pd^{II},\,150-200°}$$

159

$$H_3C-\underset{\underset{CH_3}{|}}{C}=CH-CH_2-CH_2-\underset{\underset{O}{\|}}{C}-CH_3$$

160

Metal oxides of the periodic groups VI A and IV have been used at 200° as heterogeneous catalysts for double-bond isomerization of unsaturated fatty acids[234]. Copper(II)-oxide, zinc oxide, lead(II)-oxide, and alumina, as well as the metals calcium, mercury, zinc, and iron have been used for the isomerization of double bonds in lineseed oils at elevated temperatures[235]; with the oxides, concomitant polymerization was more pronounced than was the case when the metals were used as catalysts.
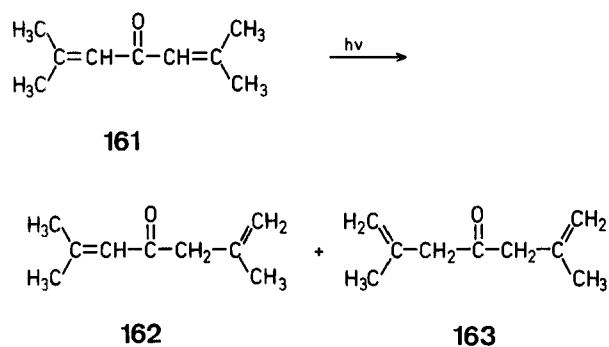
Metal carbonyls have also been found to be effective catalysts for the isomerization of double bonds in unsaturated natural oils. Thus, pentacarbonyliron isomerizes methyl oleate[236], highly unsaturated fatty acids[236], and unsaturated esters and ethers[237,238].

Anthraquinone (1-5%) has been found to catalyze the isomerization of drying oils to their conjugated isomers[239,240] at 250-275°.
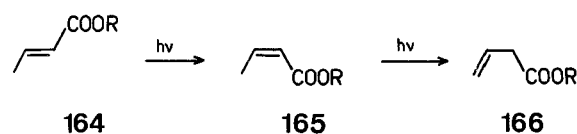
The migration of double bonds during the oxidation of drying oils is well known. The suggested mechanism involves the loss of a proton from a methylene group in a 1,4-diene system and subsequent allylic rearrangement to form a conjugated system[241,242]. Further, radicals formed during oxidation probably also induce double-bond migration. Support for this statement is given by the fact that di-t-butyl peroxide catalyzes the formation of conjugated systems in drying oils[243]. Double-bond rearrangements in various oils to form conjugated isomers may also be effected by heat alone ($\sim 320°$)[244].

The migration of double bonds in ketones is also catalyzed by acids. Thus, the isomerization of 1,2-bis-[2,3,5,6-tetramethylbenzoyl]- and 1,2-bis-[2,4,6-trimethylbenzoyl]-cyclohexenes to the corresponding 2,3-unsaturated isomers is effected in high yield by treatment with hydrochloric acid as well as with potassium hydroxide[245].

U. V. irradiation of phorone (**161**) gives the terminal isomers **162** and **163**[246].

$$H_3C\diagdown_{H_3C}\diagup C=CH-\underset{\underset{O}{\|}}{C}-CH=C\diagup^{CH_3}_{\diagdown CH_3} \quad \xrightarrow{hv}$$

161

$$H_3C\diagdown_{H_3C}\diagup C=CH-\underset{\underset{O}{\|}}{C}-CH_2-C\diagup^{CH_2}_{\diagdown CH_3} \quad + \quad H_2C\diagdown_{H_3C}\diagup C-CH_2-\underset{\underset{O}{\|}}{C}-CH_2-C\diagup^{CH_2}_{\diagdown CH_3}$$

162   **163**

Under the same conditions, methyl crotonate (**164**, R = CH$_3$) is isomerized to methyl $\varDelta^3$-butenoate (**166**, R = CH$_3$) via the cis-isomer **165** (methyl isocrotonate)[247]:

$$\diagup^{COOR}=\diagup \quad \xrightarrow{hv} \quad \diagup=\diagdown_{COOR} \quad \xrightarrow{hv} \quad \diagdiagup\diagdown_{COOR}$$

164   **165**   **166**

2.2. Isomerization of Unsaturated Cyclic Ketones

Double-bond isomerization in unsaturated cyclic ketones is subject to the same kind of conformational effects as in the case of cycloolefins. Thus, a study involving isomerization of unsaturated cyclic ketones of the 6-, 7-, 8-, and 9-membered series[248] shows that the product consists of an equilibrium mixture of the $\varDelta^2$- and $\varDelta^3$-isomers; the concentration of the individual isomers in the product depends on the conformational effects active: in the case of the six- and seven-membered rings, the conjugated isomer is the more stable, whereas in medium-sized rings in which the coplanarity required by the conjugated system is hindered due to transannular interactions, the non-conjugated isomer is the more stable[248]:

Table 2. Equilibria between $\varDelta^2$- and $\varDelta^3$-cycloalkenones[248]

| Ring size	Composition at equilibrium	
	% $\varDelta^2$-isomer	% $\varDelta^3$-isomer
6	99	1
7	73	27
8	20	80
9	<0.3	<99.7

[251] J. M. Conia, P. Amice, Bull. Soc. Chim. France **1968**, 3327.
[252] W. L. Meyer, J. F. Wolfe, J. Org. Chem. **27**, 3263 (1962).
[253] E. C. Horning, J. Org. Chem. **10**, 263 (1945).
[254] N. J. Leonard, G. C. Robinson, J. Amer. Chem. Soc. **75**, 2143 (1953).

The migration of double bonds in cyclopentenone proceeds readily in the presence of acids. Thus, 5-oxo-1,3-dimethylcyclopentene (167) upon heating with concentrated hydrochloric acid at 75–80° gives largely 3-oxo-1,4-dimethylcyclopentene (168)[249]:
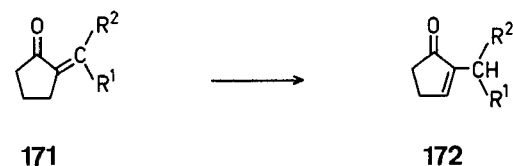

167   **168**
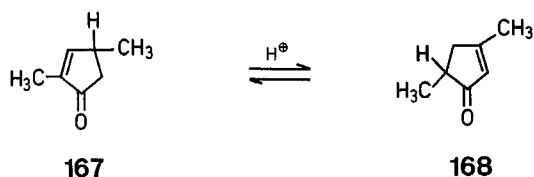
Hydrobromic acid, sulfuric acid, and aluminum chloride are less effective catalysts in this reaction, and phosphoric acid, acetic acid, and trichloroacetic acid cause only little isomerization.

Another example of acid-catalyzed isomerization is found in the equilibrium between **169** and **170**[250]:

169

170
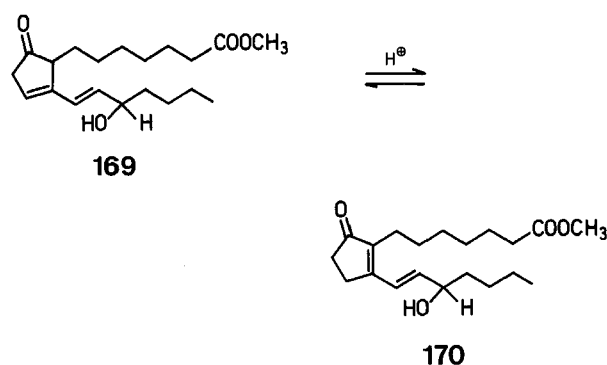
A number of 5-oxo-1-alkylcyclopentenes (**172**) may be prepared by isomerization of the corresponding 2-alkylidenecyclopentanones (**171**) in polyphosphoric acid[251]:

171   **172**

R¹ = CH₃, R² = H   53% yield
R¹ = R² = CH₃   79% yield
R¹ - R² = —(CH₂)₄ —   31% yield
R¹ = C₆H₅, R² = H   50% yield

$R^1 = CH_3, R^2 = H$ 53% yield
$R^1 = R^2 = CH_3$ 79% yield
$R^1 - R^2 = -(CH_2)_4 -$ 31% yield
$R^1 = C_6H_5, R^2 = H$ 50% yield

Although these isomerization reactions are accompanied by considerable resinification, they still represent a useful method of preparation of compounds **172**. However, the procedure is not applicable to 2,5-dibenzylidenecyclopentanone and to 2-alkylidenecyclohexanones.
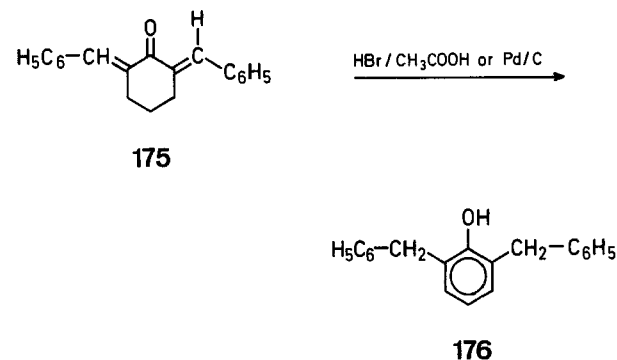
Isomerization of 2-alkylidenecyclopentanones to 5-oxo-1-alkylcyclopentenes; General procedure[251]: A mixture of the 2-alkylidene-cyclopentanone (**171**) (1 part) and polyphosphoric acid (5 parts) is heated, with vigorous stirring under a dry atmosphere, at 100° for 3 hr [in the case of 2-ethylidenecyclopentanone (**171**, $R^1 = CH_3$, $R^2 = H$), for 30 min.]. The reaction mixture is then taken up in water and extracted with ether [in the case of 2-benzylidenecyclopentanone (**171**, $R^1 = C_6H_5$, $R^2 = H$), the mixture is extracted with benzene]. The organic extract is washed with aqueous sodium hydrogen carbonate, then with water, and dried over calcium chloride. The solvent is evaporated and the residue distilled in vacuo.

As an exception in the six-membered series, pulegone (**173**) has to be mentioned. Its isomerization employing the above procedure (10 hr reaction time) gives rise to *d,l*-piperitone (**174**, 3-oxo-1-methyl-4-isopropylcyclohexene) *via* Δ^4-*p*-menthenone in 77% yield[251]:

173   **174**
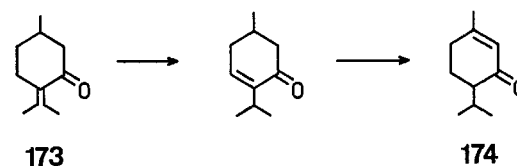
1-Acetyl-2,3,4,5,6,7-hexahydro-3a*H*-indene is isomerized by acids as well as by alkali to 1-acetyl-2,3,4,5,6,7-hexahydroindene[252].

Isomerization of 2,6-dibenzylidenecyclohexanone (**175**) by palladium on carbon[253] or with hydrogen bromide in acetic acid[254,255,256] gives 2,6-dibenzylphenol (**176**) in good yield:

175

176

[255] R. Weiss, J. Ebert, Monatsh. Chem. **65**, 399 (1935).

[256] R. H. Burnell, J. Chem. Soc. **1958**, 1307.

[257] N. J. Leonard, J. W. Berry, J. Amer. Chem. Soc. **75**, 4989 (1953).

[258] F. A. L. Anet, L. A. Bock, J. Amer. Chem. Soc. **90**, 7130 (1969).

[259] P. W. Jolly, F. G. A. Stone, K. Mackenzie, J. Chem. Soc. **1965**, 6416.

[260] R. Damico, T. J. Logan, J. Org. Chem. **32**, 2356 (1967).

[261] U.S. Patent 2837577 (1958), B. Blaser, W. Stein (Henkel & Co.); C. A. **52**, 17106 (1958).

[262] V. Macho, M. Polievka, L. Komora, Chem. Zvesti **21**, 170 (1967); C. A. **67**, 21403 (1967).

[263] Y. Makisumi, T. Sasatani, Tetrahedron Letters **1969**, 1975.

[264] G. O. Dudek, R. H. Holm, J. Amer. Chem. Soc. **84**, 2691, 2695 (1962).

[265] J. Dabrowski, J. Terpinski, Tetrahedron Letters **1965**, 1363.

[266] S. Raines, C. A. Kovacs, J. Heterocyclic Chem. **4**, 305 (1967).

[267] G. Descotes, P. Laconche, Bull. Soc. Chim. France **1968**, 2149.

[268] M. Bourillot, P. Rostang, G. Descotes, C.r. Acad. Sci. Paris **262**, 1080 (1966).

[269] P. J. Stoffel, W. D. Dixon, J. Org. Chem. **29**, 978 (1964).

[270] N. J. Leonard, D. M. Locke, J. Amer. Chem. Soc. **77**, 1852 (1955).

[271] U.S. Patent 2591367 (1952), S. H. McAllister (Shell Development Co.); C. A. **46**, 6373 (1952).

A preparatively valuable isomerization has been reported in the seven-membered series; 3,7-dibenzyl-idenecycloheptane-1,2-dione (177) is converted into 3,7-dibenzyltropolone (178) in 90% yield upon heating with palladium on charcoal in triethylene-glycol at 280° for 3 hr[157]:
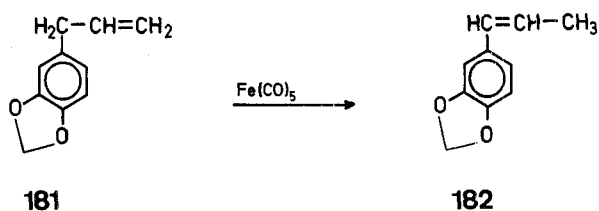

177

178
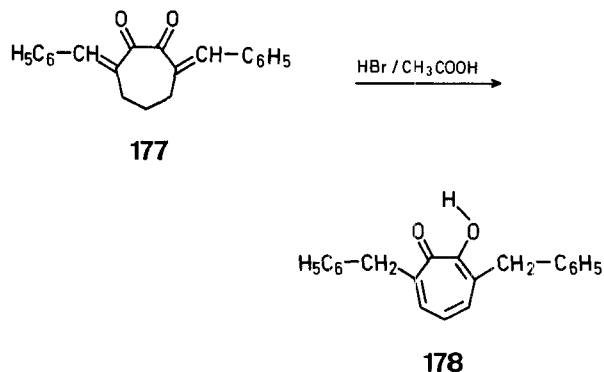
The use of hydrogen bromide in acetic acid[254] instead of palladium is less effective in this isomerization.

Compounds 179 and 180 in the ratio 17:1 are obtained upon U.V.-irradiation of either of the two isomers[258]:

179

180
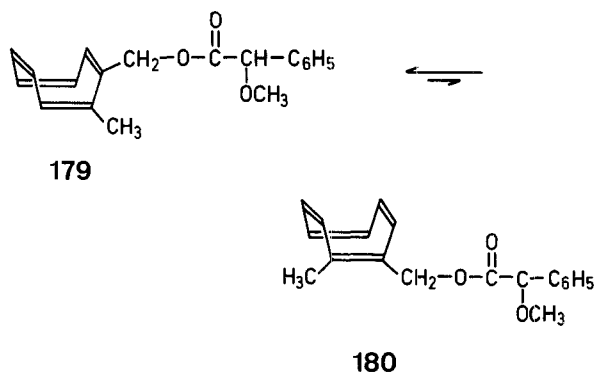
2.3. Isomerization of Olefins containing Hetero Functions other than Carbonyl Groups

Irradiation of allyl phenyl ether, allyl ethyl ether, and diallyl ether in the presence of pentacarbonyliron yields the corresponding propenyl ethers[259]. Safrole (181) is isomerized to isosafrole (182) in very good yield using pentacarbonyliron[239] in the presence of sodium hydroxide:

181 **182**

[272] H. Koch, H. van Raay, Brennstoff-Chemie 32, 161 (1951); C. A. 45, 8238 (1951).
[273] Brit. Patent 840028 (1960), Scientific Design Co.; C. A. 55, 7886 (1961).
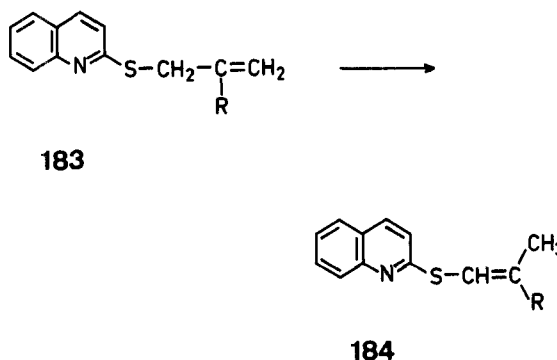
Isomerization of Safrole to Isosafrole[239]:

Method a: Safrole (500 g), pentacarbonyliron (2.5 g), and sodium hydroxide (1.6 g) are mixed in a 1000-ml flask fitted with stirrer, thermometer, and reflux condenser. The well-stirred mixture is heated at 110°, at which temperature a vigorous reaction commences, causing the temperature to rise to 180° in a few minutes. After the reaction has subsided, the mixture is cooled, 2 N acetic acid (250 ml) is added, the organic layer separated, and washed to neutrality with saturated sodium chloride solution. The product is dried and distilled; yield: 485 g (97%); b.p. 111–112°/6 mm; the product contains more than 99.5% isosafrole.

Method b: Isosafrole (50 g) is charged to a 1000-ml flask fitted with stirrer, thermometer, reflux condenser, and dropping funnel. Pentacarbonyliron (2.25 g) and sodium hydroxide (1.42 g) are added. The temperature is raised to 130° and safrole (450 g) added in the course of 30 min. The reaction mixture is maintained at 130° for 110 min. and the product isolated in the manner described above; conversion: quantitative.

The pentacarbonyliron-catalyzed isomerization of primary and secondary α,β- and β,γ-unsaturated alcohols affords aldehydes or ketones, respectively, in fair to good yields[260]. Octacarbonylcobalt is also an effective catalyst in these isomerizations[261]; for instance, allyl alcohol is isomerized to propanal under hydroformylation conditions[262] using octacarbonylcobalt as catalyst at ~150°.

Allyl sulfides of type 183 are isomerized by bases or by heating without catalyst at 200° to their propenyl isomers 184[263]:

183

184

[274] H. N. Dunning, Ind. Eng. Chem. 45, 551 (1953).
[275] U.S. Patent 2960550 (1960), M. Feller, H. M. Brennan, H. S. Seelig (Standard Oil Co.); C. A. 55, 5344 (1961).
[276] Neth. Patent 6510941 (1966), Johnson, Matthey & Co.; C. A. 64, 19408 (1966).
[277] French Patent 1460015 (1966), M. Michel (Produits Chimiques Pechiney-Saint-Gobain); C. A. 67, 57620 (1967).
[278] W. K. Meerbott, G. P. Hinds, Ind. Eng. Chem. 47, 749 (1955); U.S. Patent 2405440 (1946), N. H. Marsh (Standard Oil Development Co.); C. A. 40, 6250 (1946).
[279] S. E. Voltz, S. W. Weller, J. Phys. Chem. 59, 569 (1955).
[280] Neth. Patent 6613369 (1967), British Petroleum Co. Ltd.; C. A. 67, 53612 (1967).
[281] J. J. Phillipson, P. B. Wells, Proc. Chem. Soc. 1964, 222.
[282] V. Y. Gankin, D. P. Krinkin, D. M. Rudkovskii, Zh. Org. Khim. 2, 45 (1966); C. A. 64, 14076 (1966).
[283] U.S. Patent 3270085 (1964), C. R. Noddings, R. G. Gates (Dow Chemical Co.); C. A. 65, 15223 (1966).
[284] French Patent 1430887 (1966), I. Chauvin, G. Lefebvre (Institut Français du Petrole, des Carburants et Lubrifiants); C. A. 65, 16857 (1966).

The thermal isomerization of compounds containing C=N- or N=N-double bonds is very frequently encountered. Examples of such tautomerism reactions[264,265] are as follows:

185   **186**   **187**

188   **189**

190   **191**

192   **193**
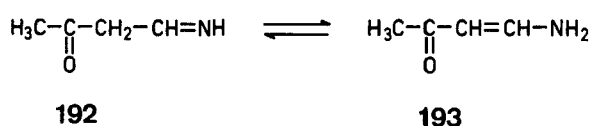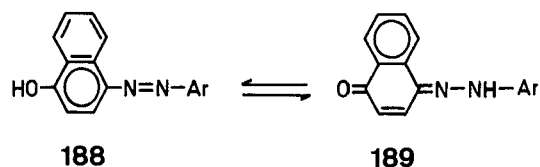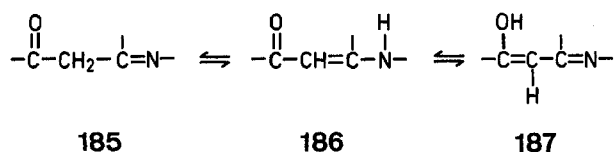
The problem of tautomerism is outside the framework of this review and thus will not be further discussed.

An example of a non-catalyzed thermal isomerization is the conversion of 2-allylbenzimidazole (**194**), which as a solid is stable at room temperature, into 2-propenylbenzimidazole (**195**) by refluxing in benzene solution[266]:

194

195
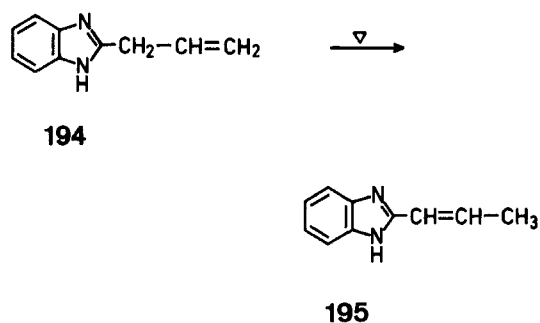
[285] Neth. Patent Appl. 6409332 (1965), British Petroleum Co.; C. A. **63**, 4080 (1965).

[286] Brit. Patent 1002394 (1965), K. H. Bourne, P. D. Holmes (British Petroleum Co.); C. A. **63**, 17893 (1965).

[287] K. Kurokawa, H. Ino, R. Aizawa, T. Amemiya, Nenryo-Kyokaishi **41**, 539 (1962); C. A. **61**, 11884 (1964).

[288] Belg. Patent 634702 (1964), E. J. Howman, R. N. Lacey, L. Turner (British Petroleum Co.); C. A. **61**, 4131 (1964).

[289] French Patent 1365885 (1964), A. Wenham, M. B. Sparke (British Petroleum Co.); C. A. **61**, 13106 (1964).

[290] L. K. Freidlin, E. F. Litvin, Neftekhimiya **4**, 374 (1964); C. A. **61**, 13106 (1964).

[291] N. B. Dobroserdova et al., Neftekhimiya **4**, 215 (1964); C. A. **61**, 2953 (1964).

[292] J. Falbe, F. Korte, Brennstoff-Chemie **45**, 103 (1964).

[293] J. F. Harrod, A. J. Chalk, J. Amer. Chem. Soc. **86**, 1776 (1964).

[294] J. Milgrom, Seventh. Inter. Conf. on Coordin. Chem. Stockholm, Sweden, 1962, 264.

[295] M. Johnson, J. Chem. Soc. **1963**, 4859.

The thermal isomerization of olefinic nitriles[267] and nitroolefins[268] in solvents such as hexamethylphosphortriamide appears to proceed *via* a mechanism involving anions and is, therefore, mechanistically related to the corresponding base-catalyzed isomerizations. In keeping with this fact, a preference for the *cis*-product is observed during the thermal isomerization[267] of compounds of type **196** and **197**:


196   **197**
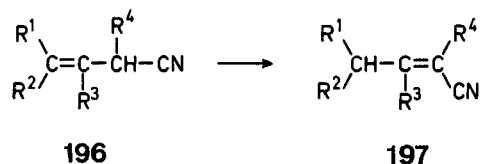
The position of the equilibrium depends strongly on the substitution of the unsaturated nitrile. Thus, double-bond deconjugation (i. e., the isomerization of **196** to **197**) is only possible if the appropriate intermediate carbanion (probably possessing structure **198**)

198
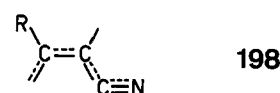
is stabilized by suitable substituents such as phenyl or phenoxy groups. The activities of solvents in promoting the thermal isomerization reaction decreases as follows:
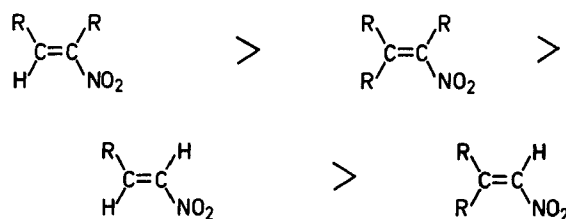
hexamethylphosphortriamide ≫ dimethyl sulfoxide > diglyme > acetonitrile > dioxan > toluene.
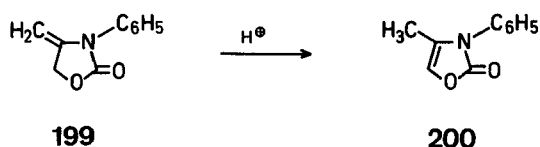
Nitroolefins are also isomerized under similar conditions[268]:
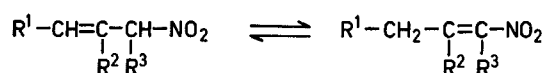
$R^1, R^2, R^3 = H, CH_3$

The following order of nitroolefin stability has been observed[268]:

2-Oxo-4-methylene-3-phenyl-tetrahydro-1,3-oxazole (**199**) upon treatment with sulfuric, *p*-toluenesulfonic, or trifluoroacetic acid is readily converted into 2-oxo-4-methyl-3-phenyldihydro-1,3-oxazole (**200**)[269]:

199   **200**

The isomerization of 1-methyl-3,5-dibenzylidene-4-piperidones (e. g. **201**) to the corresponding 1-methyl-3,5-dibenzylpyridones (**202**) using palladium on carbon as catalyst without solvent at 175 – 185° or in ethylene glycol at 195° represents a useful method of preparation of the latter class of compounds[270]:


201

202
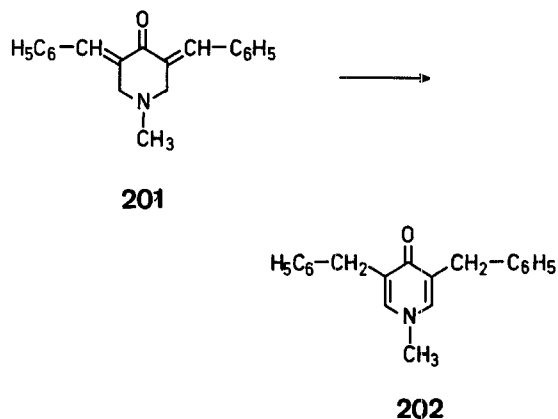
3. Isomerization of Olefins in Industrial Processes

A few examples of the large-scale application of olefin isomerization in industrial processes may serve to demonstrate the practical importance of the isomerization reactions discussed in Sections 1. and 2. of this review.

The double-bond isomerizations in unsaturated carboxylic acids are of commercial interest in improving the drying properties of oils. Further, the isomerization of olefinic hydrocarbons is employed to produce hydrocarbons better suitable for use in gasoline. Thus, the 2-olefins obtained from the sulfuric acid-catalyzed isomerization of 1-olefins are subjected to an addition reaction with alkanes to give hydrocarbons with a high octane value[271].

The hydrocarbons 2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene, but not 2-methylpentenes, are equilibrated in the presence of a cobalt-gasoline-synthesis catalyst[272]. The latter hydrocarbons may be isomerized using an alumina catalyst[272].

The commericial preparation of isoprene is carried out employing the following process[273]:

propylene → 2-methyl-1-pentene $\xrightarrow{\text{SiO}_2/\text{Al}_2\text{O}_3}$
2-methyl-2-pentene → isoprene.
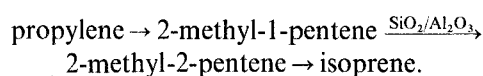
A comprehensive review of the types of catalysts used in olefin isomerization[274] has been published in 1953.

A great number of commercial isomerization reactions based on the use of transition metal catalysts has been patented[275-326] in recent years.

[296] Belg. Patent 626660 (1963), K. ALLISON (British Petroleum Co.); C. A. **60**, 8689 (1964).

[297] French Patent 1337889 (1963), P. LAFONT, G. VIVANT (Rhône-Poulenc S. A.); C. A. **60**, 2802 (1964).

[298] Belg. Patent 623503 (1963), A. G. GOBLE, M. J. HOLMES (British Petroleum Co.); C. A. **60**, 2749 (1964).

[299] R. MAUREL, M. MARCQ, J. E. GERMAIN, C. r. Acad. Sci. Paris **257**, 4196 (1963).

[300] Brit. Patent 932748 (1963), L. TURNER (British Petroleum Co.); C. A. **60**, 405 (1963).

[301] R. MAUREL, M. GIUSNET, M. MARCQ, J. E. GERMAIN, Bull. Soc. Chim. France **1966**, 3082.

[302] U. S. Patent 3310598 (1967), C. R. NODDINGS, R. G. GATES (Dow Chemical Co.); C. A. **67**, 11170 (1967).

[303] Brit. Patent 1028168 (1966), R. C. PITKETHLY, K. H. BOURNE, A. FISHER (British Petroleum Co.); C. A. **65**, 8757 (1966).

[304] J. TURKEVICH, F. NOZAKI, D. SRAMIRES, Proc. 3rd Intern. Congr. Catalysis, Amsterdam, **1**, 586 (1964).

[305] U. S. Patent 3313858 (1967), A. CLARK, B. H. ASHE, J. N. FINCH (Phillips Petroleum Co.); C. A. **67**, 11272 (1967).

[306] French Patent 1456737 (1966), M. DUBECK, L. PLONSKER, J. M. McEUEN, E. W. BRECKOFF (Ethyl Corp.); C. A. **67**, 11167 (1966).

[307] H. R. GERBERICH, W. K. HALL, J. Catalysis **5**, 99 (1966).

[308] U. S. Patent 3114785 (1963), G. L. HERVERT, C. B. LINN (Universal Oil Products Co.); C. A. **60**, 7856 (1964).

[309] French Patent 1342323 (1963), Compagnie Française de Raffinage; C. A. **60**, 7915 (1964).

[310] U. S. Patent 3268609 (1966), W. G. NIXON (Universal Oil Products Co.); C. A. **65**, 16764 (1966).

[311] U. S. Patent 3151179 (1964), F. KENNEDY, B. D. RATLIFF (Continental Oil Co.); C. A. **61**, 14525 (1964).

[312] U. S. Patent 2804490 (1957), D. H. BELDIN (Univeral Oil Products Co.); C. A. **52**, 712 (1958).

[313] U. S. Patent 2956094 (1960), M. FELLER, H. M. BRENNAN, H. S. SEELIG (Standard Oil Co.); C. A. **55**, 5932 (1961).

[314] H. KOCH, H. RICHTER, Chem. Ber. **77**, 127 (1944).

[315] U. S. Patent 2428516 (1947), H. E. DRENNAN (Phillips Petroleum Co.); C. A. **42**, 751 (1948).

[316] U. S. Patent 3236909 (1966), C. N. WINNICK (Halcon International); C. A. **64**, 14088 (1966).

[317] French Patent 1431848 (1966), Compagnie Française de Raffinage; C. A. **65**, 13462 (1966).

[318] J. B. PERI, J. Phys. Chem. **70**, 1482 (1966).

[319] J. B. PERI, Discussions Farad. Soc. **1966**, 121.

[320] U. S. Patent 3217061 (1965), G. L. HERVERT, C. B. LINN (Universal Oil Products Co.); C. A. **64**, 6491 (1966).

[321] U. S. Patent 3217059, 3217062 (1965), G. L. HERVERT, C. B. LINN (Universal Oil Products Co.); C. A. **64**, 6376, 6377.

[322] U. S. Patent 3211801 (1965), V. C. F. HOLM, D. M. BLACKBURN (Phillips Petroleum Co.); C. A. **64**, 588 (1966).

[323] U. S. Patent 3217057 (1965), L. D. MOORE, R. C. ODIOSO (Gulf Research & Development Co.); C. A. **64**, 4936 (1966).

[324] U. S. Patent 3236908 (1966), R. A. SANFORD, D. K. WUNDERLICH (Sinclair Research, Inc.); C. A. **64**, 14001 (1966).

[325] M. H. POLLEY, W. D. SCHAEFFER, W. R. SMITH, Canad. J. Chem. **33**, 314 (1955).

[326] Brit. Patent 865738 (1961), Purdue Research Foundation; C. A. **55**, 22130 (1961).