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REVIEWS

The Isomerization of Olefins Part I. Base-Catalysed Isomerization of Olefins

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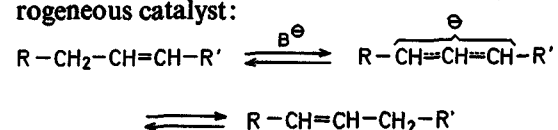
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Isomerizations of olefinic and acetylenic compounds have received much attention during the last few years both in their theoretical and in practical aspects. The methods used in isomerization of olefins (migration of the olefinic double bond) and related reactions are the subject of this review; isomerizations involving rearrangement of the carbon skeleton are not considered. Part I deals with base-catalysed isomerizations. Part II is concerned with isomerizations catalysed by acids, metal complexes, radicals, etc.

The knowledge of the conditions under which isomerization of olefins occurs, is not only valuable for the conversion of olefins to their isomers, but is an important consideration when olefins are to be prepared by any other means. Under such conditions as here described an unwanted reaction product may be formed as a result of isomerization.

1. Isomerization of Olefinic Hydrocarbons

The base-catalysed isomerization of olefins is mechanistically closely related to the chemistry of carbanions. The reaction may be effected in homogeneous solution or in the presence of a basic heterogeneous catalyst:



Base-catalysed isomerization transforms a thermodynamically less-stable olefin into a more stable one. This generally means that a terminal olefin affords the internal isomer, a non-conjugated diene the 1,3-diene, and a non-conjugated aryl-substituted olefin the corresponding styrene.

If more than two isomers participate in an equilibrium, the most stable one may be formed only slowly, so that another – less stable – isomer may be isolated after short reaction periods. For instance, terminal olefins such as 1-butene rapidly yield a mixture containing mainly the *cis*-2-isomer when allowed to react in the presence of an alcoholate. Further isomerization to the more stable *trans*-olefin as well as double bond migration towards the middle of the chain in the case of a long-chain olefin is slower^{1,2,3}.

¹ A. SCHRIESHEIM and C. A. ROWE, *Tetrahedron Letters* **1962**, 405.

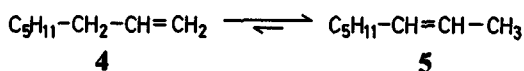
² M. D. CARR, J. R. P. CLARKE, and M. C. WHITING, *Proc. Chem. Soc.* **1963**, 333.

³ S. BANK, A. SCHRIESHEIM, and C. A. ROWE, *J. Amer. Chem. Soc.* **87**, 3244 (1965).

Lithium ethylenediamine in ethylenediamine is a homogeneous system which is very active in promoting the migration of double bonds^{23,24}. Sodium ethylenediamine is much less active (affords only 2% isomerization under reaction conditions where lithium ethylenediamine promotes essentially 100% migration)²⁵. Facile isomerization of 1,5-hexadiene (1) to 2,4-hexadiene with lithium ethylenediamine has been observed²⁶.

Sodium in isopropylamine with the addition of a small amount of allocimene was found to be effective in the isomerization of 1-octene into its internal isomers²⁷.

The preparative-scale isomerization of 1-octene (4) to 2-octene (5), however, is best carried out using the potassium derivative of dimethylsulfoxide as catalyst in dimethylsulfoxide as solvent¹³. This procedure requires only a relatively short reaction time for good yield:



Isomerization of 1-octene using the potassium derivative of dimethylsulfoxide¹³: Potassium amide (0.55 g, 10 mmol) is added to dimethylsulfoxide (7.8 g, 100 mmol) in a double-walled, three-necked 25 ml flask equipped with a condenser, a magnetic stirrer, and a gas inlet tube. The mixture is warmed under a nitrogen atmosphere at 70° until the evolution of hydrogen and ammonia ceases (~30 min.). 1-Octene is then added dropwise and with stirring, while the temperature is held at 70°. After 4 hr, ice water is added and the aqueous phase extracted three times with 40 ml petroleum ether (b. p. maximum 40°). The organic phase is washed with water until neutral, dried over calcium chloride, and fractionally distilled. The fraction distilling between 70° and 130° consists of 2-octene (65%), 1-octene (33%), and 3-octene (2%); conversion: 67%; yield of 2-octene: 65% of theory, 97% calculated on conversion of 1-octene.

Using potassium *t*-butoxide as catalyst in the solvents dimethyl sulfoxide or pentane, good yields of 2-octene are only obtained after very long reaction times.

Potassium methoxide in methanol²⁸ and potassium *t*-butoxide in *t*-butanol²⁹ were used in the study of the equilibrium between 1-phenyl-1-butene and 1-phenyl-2-butene. In this case, the conjugated isomer is only slightly more stable; at 165°, it makes up 82% of the equilibrium mixture.

¹¹ A. SCHRIESHEIM, J. HOFMANN, and C. A. ROWE, *J. Amer. Chem. Soc.* **83**, 3731 (1961).

¹² D. J. CRAM, *J. Amer. Chem. Soc.* **83**, 3768 (1961).

¹³ F. ASINGER, B. FELL, and P. KRINGS, *Chem. Ber.* **99**, 1737 (1966); describes isomerization of octenes in dimethyl sulfoxide using: potassium amide, sodium hydride, and potassium *t*-butoxide.

¹⁴ For a review see: D. MARTIN, A. WEISE, and H. J. NICLAS, *Das Lösungsmittel Dimethylsulfoxid*, *Angew. Chem.* **79**, 340 (1967).

¹⁵ U. S. Patent 3 217 050 (1966), Esso Research and Engineering Co., A. SCHRIESHEIM and C. A. ROWE; *C. A.* **64**, 3348 (1966).

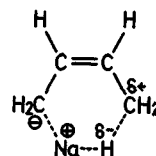
1.1.2. Isomerization of Linear Olefins on Heterogeneous Basic Catalysts

Alkali metals on a (mostly inorganic) carrier material, e.g. alkali graphites, metal amides, and organo-alkali metal compounds, are heterogeneous basic catalysts which have been used in the isomerization of linear olefins.

As is the case in base-catalysed isomerization in homogeneous solution, the isomerization effected on basic heterogeneous catalysts is reversible.

Structure and stability of the carbanion intermediate formed on proton abstraction from the olefin, together with kinetic effects, appear to be important factors controlling the isomerization reaction. Solvent effects and the nature of the catalyst also play an important role.

In the isomerization of 1-butene using a high-surface sodium-on-alumina catalyst at 30°, the less stable *cis*-2-butene is formed four times faster than the *trans*-isomer³⁰. This fact may be explained by the greater stability of the intermediate *cis* allylic carbanion over that of the *trans* form³, by the stabilization of the *cis*-anion by an additional resonance structure³⁰,



(both effects resulting in an increased concentration of the *cis*-carbanion), and by the different rates of protonation of the *trans* and *cis*-carbanions in the 1 and 3 positions, respectively³⁰.

In the isomerization of 1-butene and 1-pentene, dispersed sodium on alumina has proved to be a more effective catalyst than sodium on silica or sodium on

¹⁶ U. S. Patent 3 270 084 (1966), Esso Research and Engineering Co., A. SCHRIESHEIM, C. A. ROWE, and W. BARTOK; *C. A.* **65**, 18397 (1966).

¹⁷ J. UGESTAD and O. A. ROCKSTAD, *Acta Chem. Scand.* **18**, 474 (1964).

¹⁸ see also: C. AGAMI, *Bull. Soc. Chim. France* **1968**, 1209.

¹⁹ A. I. SHATENSTEIN, L. N. VASILEVA, N. M. DYKHNO, and E. A. IZRAILEVICH, *Doklady Akad. Nauk SSSR* **85**, 381 (1952).

²⁰ E. A. RABINOVICH, I. V. ASTAFEV, and A. J. SHATENSTEIN, *Zh. Obshch. Khim.* **32**, 748 (1962).

²¹ C. R. HAUSER, P. S. SKELL, R. D. BRIGHT, and W. B. RENFROW, *J. Amer. Chem. Soc.* **69**, 589 (1947).

²² E. GROVENSTEIN, S. CHANDRA, C. E. COLUM, and W. E. DAVIS, *J. Amer. Chem. Soc.* **88**, 1275 (1966).

²³ L. REGGEL, R. A. FRIEDEL, and I. WENDER, *J. Org. Chem.* **22**, 891 (1957).

²⁴ L. REGGEL, S. FRIEDMAN, and I. WENDER, Abstracts of Papers given at the 129th Meeting of the American Chemical Society, Dallas, 1956.

²⁵ L. REGGEL, S. FRIEDMAN, and I. WENDER, *J. Org. Chem.* **23**, 1136 (1958).

²⁶ B. S. TYAGI, B. B. GHATGE, and S. C. BHATTACHARYYA, *J. Org. Chem.* **27**, 1430 (1962).

sodium carbonate³⁰. Although it exhibits similar activity, lithium on alumina appears to be less selective than sodium on alumina³⁰.

The high-surface sodium-on-alumina catalyst may be prepared by adding ~10% sodium to dry alumina in a nitrogen atmosphere at 150–200° with agitation using a sweep-type stirrer³⁰. The catalyst thus obtained is considerably more active than a sodium-on-alumina catalyst prepared *in situ* in a rotating autoclave.

Sodium on γ -alumina with a trace of ferric oxide added to the dispersed catalyst as a promoter is very active in the isomerization of allylbenzene and 1-phenyl-2-butene³¹. A 98% conversion of 1-pentene to 2-pentene has been reported using a catalyst containing a small amount of calcium hydroxide or sodium carbonate as promoter for the ferric oxide.³²

Potassium graphite also exhibits high catalytic activity in the isomerization of 1-pentene to its *cis*- and *trans*-2-isomers³³.

Other catalysts which have been employed in the isomerization of Δ^1 -olefins into the more stable Δ^2 -isomers are sodium/anthracene³⁰, fluorenylsodium³⁴, phenylsodium³⁴, various alkylsodium compounds³⁴, and metal amides like calcium diamide³⁵.

The use of heterogeneous catalysts in the isomerization reaction has been reviewed³⁶ in 1962.

1.2. Isomerization of Cyclic Olefins

The principles applicable to the open-chain aliphatic series are also valid for the corresponding cyclic systems. In addition, some effects are peculiar to the cyclic aliphatic series:

The possibility of formation of Hückel-aromatic systems (e. g., the cyclopentadienyl anion) explains the extremely high isomerization tendency of some cyclic compounds.

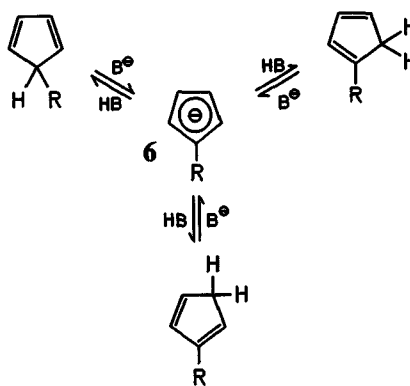
The spacial orientation of the hydrogen atoms in some cyclic systems (e. g., cycloheptatriene) allows them to migrate via 1,5-shifts. Such reactions are thermally initiated, and because of this, will be discussed in Part II of this review.

Conformational effects exert great influence upon the equilibrium between the various isomers; this effect may be particularly observed in medium-sized rings.

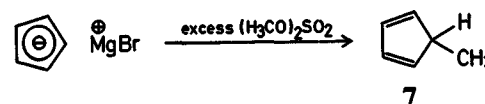
Cyclopropenes may be prepared in strongly alkaline medium. In accordance with Hückel's rule, formation of the cation gives rise to a stable system; loss of a proton, however, gives rise to a very unstable „antiaromatic“ anion.

Base-catalysed isomerizations of cyclobutenes not carrying substituents permitting exocyclic shifts of the double bond have not yet been studied. The same is true for the cyclopentene system.

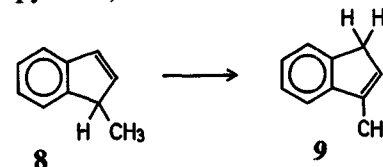
Substituted cyclopentadienes are so rapidly isomerized under basic conditions (due to the ease of formation of the highly stabilized cyclopentadienyl anions **6**) that measurement of the rates was impossible³⁷:



Cyclopentadienes substituted in the 5-position may only be isolated if all traces of bases are completely avoided during the preparation and workup³⁸. The only practical method of preparation at present is the alkylation of cyclopentadienylmagnesium bromide (e. g., methylation using dimethyl sulfate to yield 5-methylcyclopentadiene, **7**)³⁸:



Analogously, 1-methylindene (**8**) is only stable in moderately acidic and neutral solutions; it rearranges completely to 3-methylindene (**9**) under the influence of a basic catalyst³⁹ (e. g., triethylamine in pyridine):



²⁷ L. DAVID, A. HERGOMARD, and S. VINCENT, *Compt. Rend. Acad. Sci. Paris [C]* **266**, 338 (1968).

²⁸ L. BATEMAN and J. I. CUNNEEN, *J. Chem. Soc.* **1951**, 2283.

²⁹ W. PROELL, *J. Org. Chem.* **16**, 178 (1951).

³⁰ W. O. HAAG and H. PINES, *J. Amer. Chem. Soc.* **82**, 387 (1960).

³¹ U. S. Patent 3 257 415 (1966), Standard Oil Co. (Indiana), T. M. O'GRADY, R. M. ALM, M. C. HOFF; *C. A.* **65**, 12106 (1966).

³² U. S. Patent 3 260 679 (1966), Standard Oil Co. (Indiana), T. M. O'GRADY, A. N. WENNERBERG; *C. A.* **65**, 10494 (1966).

³³ D. M. OTTMERS and H. F. RASE, *Ind. Eng. Chem. Fundamentals* **5**, 302 (1966).

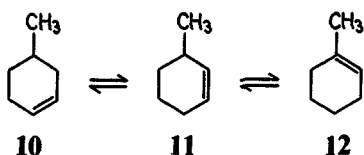
³⁴ A. A. MORTON and E. J. LANPHER, *J. Org. Chem.* **20**, 839 (1955).

³⁵ B. A. KAZANSKII and I. V. GOSTUNSKAYA, *Kataliz v Vysshei Shkole, Min. Vysshego i Srednego Spets. Obrazov. SSSR, Tr. 1. Mezhoz. Soveshch. po Katalizu 1958*, Part 1, 341 (Publ. 1962); *C. A.* **59**, 6237 (1963).

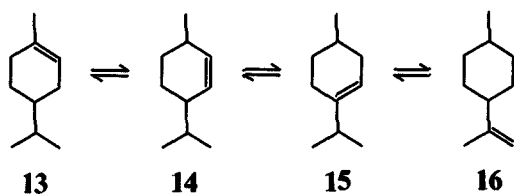
The same is true for 1-benzylindene³⁹. In these isomerizations, 1,4-diaza-bicyclo[2.2.2]octane is even more effective as catalyst than triethylamine⁴⁰.

Interestingly, the proton transfer in 1-(3-)substituted indenenes is completely intramolecular and stereospecific⁴⁰ when triethylamine or 1,4-diaza-bicyclo[2.2.2]octane are used as catalyst in pyridine solution. When dimethylsulfoxide is used as solvent, however, less stereospecificity is observed, and with potassium t-butoxide as catalyst in t-butanol as solvent, rapid racemization of the 1-substituted indenenes occurs.

The six-membered cyclic olefins have been extensively studied. Isomerization of 3-methylcyclohexene (10) in a homogeneous dimethylsulfoxide solution employing potassium t-butoxide as base⁴¹ produces a mixture of the isomers 10, 11, and 12:

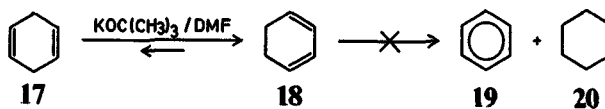


Upon refluxing either one of the four isomeric p-menthenes (13–16) for several days in the presence of a sodium-organosodium catalyst, mixtures of the four isomers⁴² containing 15 as major component and traces only of compounds 14 and 16 are obtained:

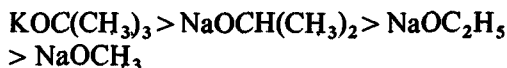


The two isomeric cyclohexadienes (17 and 18) exhibit no essential difference in their thermodynamical stabilities⁴³; the equilibrium mixture obtained by starting with the 1,4-isomer (17) in the liquid phase at temperatures above its atmospheric boiling point, using an alkali metal alkoxide without solvent, contains 31.1% of the 1,4-isomer (17) and 68.9% of the 1,3-isomer (18)⁴⁴. The isomerization is frequently accompanied by disproportionation of 18 into benzene (19) and cyclohexene (20). This side reaction may be avoided by working in aprotic solvents such as

dimethylformamide or pyridine⁴⁵. Using potassium t-butoxide as catalyst at 50°, an almost 70% conversion of 17 into 18 is achieved within a few hours⁴⁵:



The conversion decreases with decreasing base strength of the catalyst used:

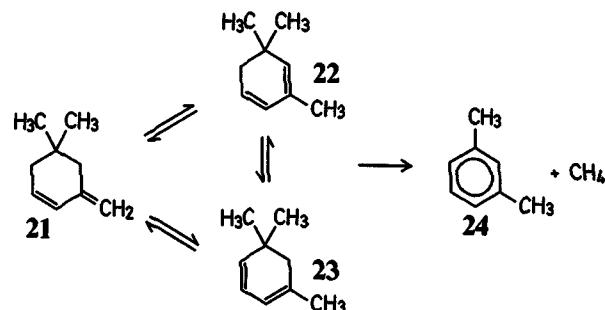


The rate of conversions is dependent upon solvent:

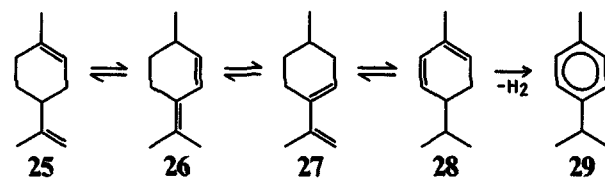


Sodium ethoxide in ammonia has also been used⁴⁶ for this isomerization.

The isomerization of 3-methylene-5,5-dimethylcyclohexene (21) carried out in refluxing xylene in the presence of a sodium-benzylsodium catalyst gives rise to the two isomeric trimethylcyclohexadienes 22 and 23; after a reaction time of 4 hours, i. r. analysis of the mixture shows that these products are present to the extent of 19%. However, the cyclohexadienes 22 and 23 are not stable under the conditions employed. On prolonged refluxing (24 hr), the equilibrium mixture is completely transformed into 1,3-dimethylbenzene (24) and methane⁴⁷:



The isomerization of d-limonene (25) at reflux temperature on a sodium-organosodium catalyst (obtained from sodium and 2-chlorotoluene) yields the isomeric products 25–28. The isomerization is accompanied by a slow dehydrogenation producing p-cymene (29) as the ultimate product⁴⁸:



³⁶ H. PINES and L. A. SCHAAP, *Adv. Catalysis* **12**, 117 (1962).

³⁷ S. MCLEAN and P. HAYNES, *Tetrahedron Letters* **1964**, 2385.

³⁸ V. A. MIRONOV, E. V. SOBOLEV, and A. N. ELIZAROVA, *Tetrahedron Letters* **1963**, 1939.

³⁹ G. BERGSON and A. M. WEIDLER, *Acta Chem. Scand.* **17**, 862 (1963).

A. M. WEIDLER, *Acta Chem. Scand.* **17**, 2724 (1963).

⁴⁰ A. M. WEIDLER and G. BERGSON, *Acta Chem. Scand.* **18**, 1487 (1964).

see also: L. OHLSSON and I. WALLMARK, *Acta Chem. Scand.* **20**, 750 (1966).

⁴¹ H. TURKSMA, H. STEINBERG, and T. H. J. DEBOER, *Rec. Trav. Chim.* **82**, 1057 (1963).

⁴² H. PINES and H. E. ESCHINAZI, *J. Amer. Chem. Soc.* **78**, 1178 (1956).

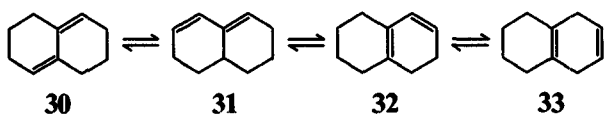
⁴³ R. B. BATES, R. H. CARNIGHAN, and C. E. STAPLES, *J. Amer. Chem. Soc.* **85**, 3030 (1963).

⁴⁴ U.S. Patent 2 316 136 (1943), DuPont, N. TURNBULL; C. A. **37**, 5420 (1943).

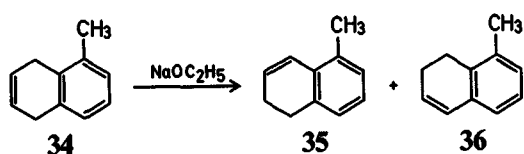
⁴⁵ T. YAMAGUCHI et al., *Chem. & Ind.* **1967**, 759.

Potassium *t*-butoxide at its decomposition temperature (250–300°) also catalyzes the isomerization, although dehydrogenation leading to the aromatic system is more pronounced⁴⁹.

In the hexahydronaphthalene series, *transoid* dienes are more stable than *cisoid* dienes, and the relative stabilities of the two systems containing both double bonds in one ring are similar to those of the corresponding cyclohexadienes 17 and 18. Thus, treatment of either $\Delta^{1,8}$ -hexahydronaphthalene (31) or $\Delta^{2,9}$ (¹⁰)-hexahydronaphthalene (33) with potassium *t*-pentyloxyde in *t*-pentanol as solvent (reaction time: 24 hr) produces an equilibrium mixture which contains 30 (53.7%), 31 (25.5%), 32 (14.1%), and 33 (6.4%)⁴³:

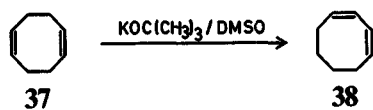


Upon heating 1-methyl-6,8-dihydronaphthalene (34) in ethanol in the presence of sodium ethoxide, a mixture of the isomers 35 and 36 in almost equimolar amounts is obtained⁵⁰:

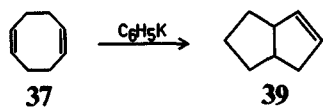


In the series of unsaturated cyclic seven-membered hydrocarbons, base-catalyzed isomerizations have not been investigated.

The isomerization of cycloocta-1,5-diene (37) at 70° using potassium *t*-butoxide as catalyst in dimethyl sulfoxide as solvent⁵¹ (1 hr) results in essentially quantitative conversion to the conjugated isomer 38:



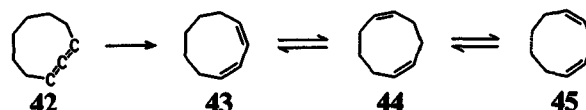
When the isomerization of 37 is carried out in heptane solution at 175–220° using a phenylpotassium catalyst prepared *in situ* from potassium and anisole in the presence of propene, the reaction takes a different course and Δ^2 -bicyclo[3.3.0]octene (39) is isolated as the main product⁵²:



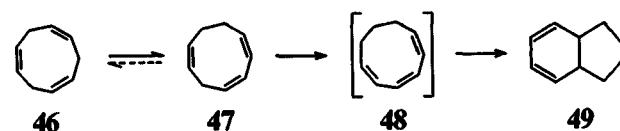
Cycloocta-1,3,6-triene (40) has been isomerized to the 1,3,5-triene (41) by treatment with potassium *t*-butoxide in *t*-butanol at 100° (18 hr)⁵³:



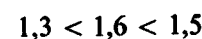
Isomerization of cyclonona-1,2-diene (42) (possessing an allene structure) by heating at 70° for 1 hour in *t*-butanol as solvent in the presence of potassium *t*-butoxide⁵¹ yields the conjugated cyclonona-1,3-diene (43) which in turn, upon prolonged reaction time, undergoes equilibration to afford smaller quantities of the non-conjugated isomers 44 and 45:



The isomerization of cyclonona-1,4,7-triene (46) using potassium *t*-butoxide in dimethylsulfoxide at 25–50° yields the 1,3,6-isomer (47) as the main product after 5–7 minutes. Upon extension of the reaction time to 60 minutes, compound 47 is further isomerized to $\Delta^{2,4}$ -bicyclo[4.3.0]nonadiene (49) via the 1,3,5-isomer (48)⁵⁴:



Medium and large-ring cycloalkadienes (C_{10} – C_{26}) are readily isomerized by calcium amide⁵⁵ or by a dispersion of potassium on alumina⁵⁶. The position of the equilibrium depends upon the ring size. In 12-membered ring systems, the 1,5-isomer is most stable; in the 13-membered ring the stability of the isomers increases in the following order:



In the case of rings larger than C_{13} , the conjugated 1,3-isomer is always the most stable; in addition, the diametrical dienes (double bonds in opposite positions of the ring) are preferred in the case of the 14-, 18-, 22-, and 26-membered rings. The 16-, 20-, and 24-membered cyclic dienes exhibit a second maximum of stability (besides in the conjugated form) in the „next-to-diametrical“ structure. Consideration of the Pitzer strain in the different isomers offers an explanation for these facts⁵⁶.

⁴⁶ Brit. Patent 1 033 760 (1966), M. AMAGASA, T. YAMAGUCHI, M. TANAKA; C. A. 65, 7075 (1966).

⁴⁷ H. PINES and H. E. ESCHINAZI, J. Amer. Chem. Soc. 78, 5950 (1956).

⁴⁸ H. PINES, J. A. VESELY, and V. N. IPATIEFF, J. Amer. Chem. Soc. 77, 347 (1955).

H. PINES and H. E. ESCHINAZI, J. Amer. Chem. Soc. 77, 6314 (1955).

⁴⁹ H. PINES and L. SCHAAP, J. Amer. Chem. Soc. 79, 2956 (1957).

⁵⁰ W. HÜCKEL and C. M. JENNEWEIN, Chem. Ber. 95, 350 (1962).

⁵¹ D. DEVAPRABHOKARA, C. G. CARDENAS, and P. D. GARDNER, J. Amer. Chem. Soc. 85, 1553 (1963).

⁵² U.S. Patent 3363016 (1968), Phillips Petroleum Co., P. R. STAPP; C. A. 68, 86892 (1968).

Isomerization of Cycloalkadienes and Analysis of the Equilibrium Mixture⁵⁶: A solution of the cycloalkadiene (2g) in heptane (100 ml) is added to a dispersion of potassium (1.5g) on alumina (10 g) at 25° (The catalyst is prepared according to the procedure of Haag and Pines³⁰ mentioned in chapter 1.1.2.; potassium is substituted for sodium). The mixture is stirred in a nitrogen atmosphere. The resultant equilibrium mixture is analysed by the following procedure: samples (18 ml) taken from the mixture at intervals are poured into propanol and ozonolyzed. Reduction with sodium borohydride and acetylation of the products with subsequent analysis by gas-liquid chromatography³⁷ allows calculation of the isomer distribution.

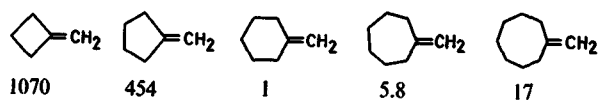
The reduction of some of the conjugated medium-ring and macrocyclic dienes to give the cyclomonoolefins, observed as a side reaction of the isomerization may, under certain conditions, be employed for the preparation of the cyclomonoolefins⁵⁸.

1.3. Isomerization of Exocyclic Olefins

Endocyclic olefins are as a rule more stable than their exocyclic isomers. The relative stabilities of these two olefin types are, however, quite different in the C₅- and C₆-ring derivatives. On this account, it is only reasonable to compare the relative stabilities of the exocyclic isomers of the C₅-series with those of the C₆-series.

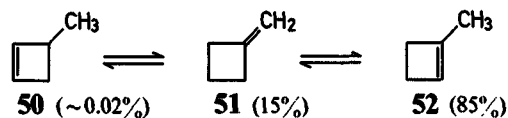
An explanation in terms of internal strain due to eclipsing hydrogen atoms of the methylene groups and steric interaction of vinylic and neighbouring equatorial hydrogen atoms has been proposed⁵⁹.

The relative rates of isomerization of methylenecycloalkanes (C₄–C₈) correspond to those of base-catalysed bromination of the cyclic ketones⁶⁰. The rates of isomerization of the four- to eight-membered methylenecycloalkanes (isomerization effected using potassium t-butoxide in dimethyl sulfoxide at 55°) are listed below⁶⁰:



The position of the equilibrium between methylenecyclobutene (**51**) and its endocyclic isomers (**50** and **52**) has been determined by isomerizing any one of the three isomers using a sodium-alumina catalyst

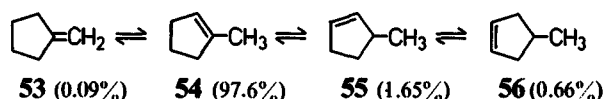
(in the case of compound **50**, in 2,4-dimethylpentane as solvent at 5°; in the case of compounds **51** and **52**, without solvent at 25°)⁶¹:



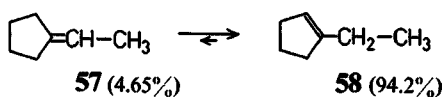
Isomerization of purified (commercially available) **51** at a temperature below 5° using sodium on alumina as catalyst without solvent represents a convenient procedure for the preparation of 1-methylcyclobutene (**52**)⁶².

1-Methylcyclobutene⁶²: In a typical catalyst preparation, alumina (12g; 100 mesh, pretreated at 300–320° under nitrogen for 24 hr) is introduced into a three-necked flask equipped with a condenser, a dropping funnel, and a mechanical stirrer provided with a semi-circular impeller. The system is purged with nitrogen and the alumina heated to 140°, at which point sodium (2 g) is added with stirring. Mixing at 140° is continued for 20 min, and the flask containing the black catalyst cooled to 2–3° in an ice-water bath. Methylenecyclobutane (50g; freshly distilled over sodium to avoid deactivation of the catalyst) is added in one portion to the flask. The flow of nitrogen is reduced to a minimum and ice water is circulated through the condenser. The temperature of the reaction mixture is held below 5° and stirring is continued for 2 hr. At the end of this period the supernatant liquid is quickly decanted into a precooled flash. The rest of the product, which is partly absorbed on the catalyst, is recovered by distillation at 100 mm into a Dry Ice-acetone trap. The product (47g, 94% recovery) contains 86% 1-methylcyclobutene. Fractional distillation affords a sample of 99% purity; b. p. 37.3°; n_D²⁰: 1.4081.

Isomerization of 1-methylcyclopentene (**54**) at 25° using a sodium-on-alumina catalyst without solvent gives products similar to those of the analogous isomerization in the four-membered series; the following mixture of isomers is obtained⁶¹:



ω -Methyl substitution brings about little change in the distribution of the corresponding isomers: 1-ethylcyclopentane (**58**) is the major component of the equilibrium mixture; ethylidene cyclopentane (**57**) is present to the extent of a few percent whereas the other isomers, especially vinylcyclopentane, are found in only very small amounts⁶¹:



The same isomerization has also been carried out using calcium amide⁶³ or arylsodium⁶⁴ as catalyst.

⁸³ A. C. COPE and F. A. HOCHSTEIN, *J. Amer. Chem. Soc.* **72**, 2515 (1950).

A. C. COPE, A. C. HAVEN, F. L. RAMP, and E. R. TRUMBULL, *J. Amer. Chem. Soc.* **74**, 4867 (1952).

⁸⁴ J. W. H. WATTHEY and S. WINSTEIN, *J. Amer. Chem. Soc.* **85**, 3715 (1963).

D. S. GLASS, J. W. H. WATTHEY, and S. WINSTEIN, *Tetrahedron Letters* **1965**, 377.

⁵⁵ U.S. Patent 3360578 (1967), Columbia Carbon Co., S. F. CHAPPEL; *C.A.* **68**, 86889 (1968).

⁵⁶ A. J. HUBERT and J. DALE, *J. Chem. Soc. [C]* **1968**, 188.

⁵⁷ A. J. HUBERT, *J. Chem. Soc.* **1963**, 4088.

⁵⁸ A. J. HUBERT, *J. Chem. Soc. [C]* **1967**, 2149.

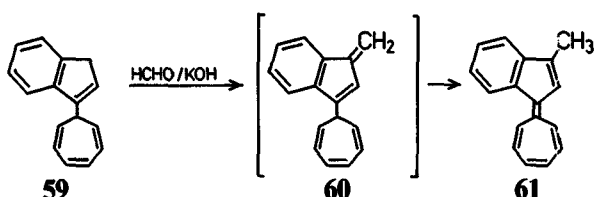
⁵⁹ H. C. BROWN, J. H. BREWSTER, and R. S. FLETCHER, *J. Amer. Chem. Soc.* **76**, 467 (1954).

E. J. COREY and R. A. SNEEN, *J. Amer. Chem. Soc.* **77**, 2505 (1955).

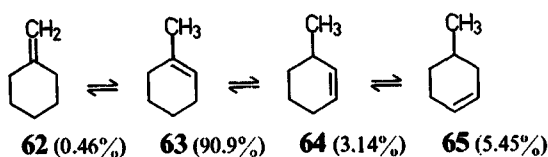
R. B. TURNER and R. H. GARNER, *J. Amer. Chem. Soc.* **80**, 1424 (1958).

A dispersion of potassium amide on alumina effects only slow isomerization of 3-benzylidene to 3-benzylideneindane⁶⁵; the acid-catalyzed isomerization of this system, however, proceeds faster (see Part II of this review).

The isomers formed in the preparation of some benzylideneindenes (benzofulvenes) have been investigated by chemical⁶⁶ and spectrometric methods⁶⁷. In the preparation of 3-methyl-1-cycloheptatrienylideneindene (**61**) by reaction of 3-(cycloheptatrien-7-yl)-indene (**59**) with formaldehyde in the presence of an aqueous-methanolic solution of potassium hydroxide, the intermediate compound **60** is isomerized so fast to **61** that the former can not be detected in the reaction mixture⁶⁷:

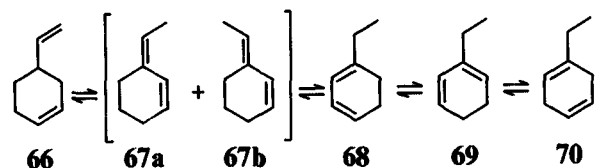


Equilibration of methylenecyclohexane (**62**), or of the isomeric methylcyclohexenes (**63**, **64**, **65**), at 25° using sodium on alumina as catalyst without solvent gives rise to the following mixture⁶¹:



The analogous reaction of 1-ethylcyclohexene leads to an equilibrium mixture containing 1-ethylcyclohexene (82.4%) and ethylidenecyclohexane (9.54%)⁶¹.

The base-catalyzed isomerization of (readily available) 4-vinylcyclohexene (**66**, dipentene) in homogeneous solution using the system potassium t-butoxide/dimethyl sulfoxide may be applied to the large-scale preparation of 3-ethylidenecyclohexene (*cis* and *trans*, **67a** and **b**; 40% yield)⁶⁸. The reaction is carried out in an autoclave at 100° (75 hr); compounds **67a** and **67b** are readily isolated from the resultant mixture by fractional distillation because of the considerable difference between their boiling points and those of the other isomers. Under milder reaction conditions (55°), the compounds listed below may be isolated after a reaction time of 50 min⁶⁸:



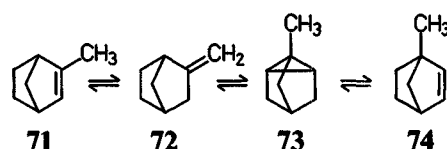
⁶⁰ A. SCHRIESHEIM, R. J. MULLER, and C. A. ROWE, *J. Amer. Chem. Soc.* **84**, 3164 (1962).

⁶¹ J. HERLING, J. SHABTAL, and E. GIL-AV, *J. Amer. Chem. Soc.* **87**, 4107 (1965).

Upon treatment with lithium dimethylamide in hexamethylphosphortriamide at elevated temperatures, the isomerization of 3-vinylcyclohexene is accompanied by a disproportionation into ethylbenzene and ethylcyclohexene.

Similar results are obtained in the isomerization of 1-methyl-4-isopropenylcyclohexene using potassium t-butoxide in dimethyl sulfoxide⁶⁸ (compare with **25** under paragraph 1.2.).

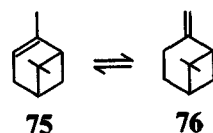
A base-catalyzed hydrogen shift in the bicyclic series is more frequently accompanied by rearrangements of the carbon skeleton than is the case in the monocyclic series. For example, 2-methylenebicyclo[2.2.1]heptane (**72**) isomerizes in the presence of sodium-toluene catalyst at 170° (24 hr) to yield ~20% 2-methyl- Δ^2 -bicyclo[2.2.1]heptene (**71**)⁶⁹. Upon prolongation of the reaction time, considerable amounts of the tricyclic compound **73** may also be obtained, and on increasing the reaction temperature to 230–280°, a fourth isomer (**74**) is found in small quantities among the products:



On account of ring strain, the endocyclic isomer **71** is less stable than the exocyclic isomer **72**.

The equilibration of compounds **71** and **72** starting with the isomer **71** has also been carried out by refluxing the hydrocarbon in the presence of calcium amide⁷⁰.

Partial isomerization of α -pinene (**75**) to β -pinene (**76**) has been effected employing a sodium-on-sodium-carbonate catalyst⁷¹ without solvent at 180–200° and 50–300 mm, and with potassium hydroxide in dimethyl sulfoxide⁷² at 110–225°:



⁶² J. SHABTAL and E. GIL-AV, *J. Org. Chem.* **28**, 2893 (1963).

⁶³ N. A. BELIKOVA et al., *Zh. Org. Khim.* **1**, 506 (1965).

⁶⁴ J. SHABTAL, *Tetrahedron Letters* **1964**, 467.

⁶⁵ A. J. HUBERT and H. REIMLINGER, *J. Chem. Soc. [C]* **1969**, in press.

⁶⁶ J. THIELE and R. MERCK, *Liebigs Ann. Chem.* **415**, 257 (1918).

⁶⁷ H. PRINZBACH, D. SEIP, and G. ENGLERT, *Liebigs Ann. Chem.* **698**, 57 (1966); additional references may be found in this publication.

⁶⁸ S. BANK, C. A. ROWE, A. SCHRIESHEIM, and L. A. NASLUND, *J. Org. Chem.* **33**, 221 (1968).

⁶⁹ M. BLANCHARD, M. GUISET, and R. MAUREL, *Compt. rend.* **258**, 2593 (1964).

For a detailed study of the isomerization rates of some bicyclic olefins, see: S. BANK, C. A. ROWE, A. SCHRIESHEIM, and L. A. NASLUND, *J. Amer. Chem. Soc.* **89**, 6897 (1967).

2. Isomerization of Olefins Containing Hetero Atoms

2.1. Isomerization of Olefins Containing Carbonyl or Cyano Functions

It has been demonstrated in the preceding chapter that dienes and aryl-substituted alkenes normally isomerize to yield predominantly the conjugated isomer. In the case of unsaturated aldehydes, ketones, carboxylic acids, carboxylic acid esters, carboxylic acid amides, and nitriles, conjugation is likewise the most important factor in determining the equilibrium position⁷³. In general, the equilibrium lies on the side of the conjugated isomer:

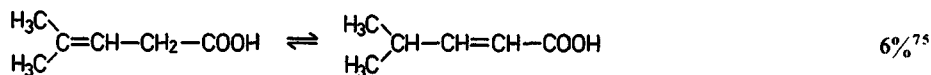
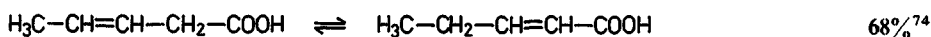
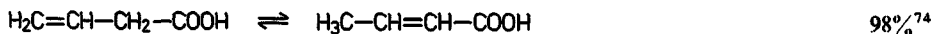


However, if two γ -alkyl groups are present, the β,γ -unsaturated isomer is favored in the equilibrium²⁸:

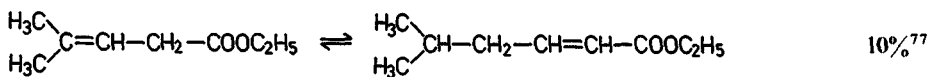
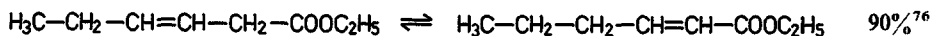


The influence of a γ -methyl substituent upon the position of the equilibrium is demonstrated by the examples listed below; the percentages given refer to the conjugated isomer present in the equilibrium mixture.

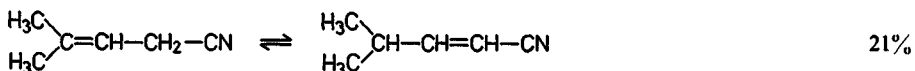
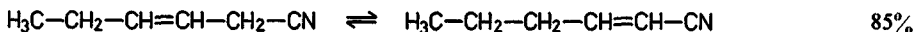
Unsaturated acids (equilibrated at 100° using 10 equivalents of 25% aqueous potassium hydroxide):



Unsaturated esters (equilibrated at 25° using sodium ethoxide in carefully dried ethanol):

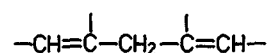


Unsaturated nitriles (same conditions as with the esters)⁷⁸:



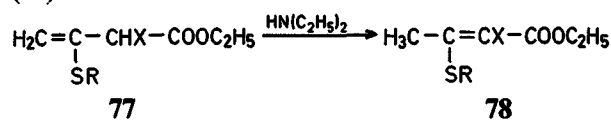
In the base-catalyzed isomerization of long-chain fatty acids, a fairly regular distribution of the double bond along the chain is observed; a slight preference for the α,β -position and the $\omega-2, \omega-1$ -position may be noted. Oleic acid has been isomerized⁷⁹ in this way in an aqueous solution of potassium hydroxide or sodium carbonate under pressure at temperatures above 300°. With potassium hydroxide as catalyst, degradation of the chain occurs under severe reaction conditions.

Alkaline isomerization of non-conjugated dienoic acids containing the group



generally gives rise to the conjugated isomers. This reaction has been used as an analytical procedure in determining the 1,4-diene system⁸⁰.

Upon treatment with diethylamine, esters of the type **77** are smoothly converted into their Δ^2 -isomers (**78**)⁸¹:



X = Cl, SC₂H₅

The methyl ester of 3-phenyl-2-diphenylmethylcyclopropene-1-carboxylic acid (**79**) may be isomerized to the more stable non-conjugated exocyclic isomer

⁷⁰ N. A. BELIKOVA et al., *Zh. Org. Khim.* **1**, 506 (1965); *C. A.* **63**, 2906 (1965).

⁷¹ U.S. Patent 3325 553 (1967), J. M. DERFER; *C. A.* **67**, 108794 (1967).

⁷² U.S. Patent 3264 362 (1966), Union Bag-Camp Paper Corp., R. L. WEBB; *C. A.* **65**, 15436 (1966).

⁷³ H. GILMAN, *Organic Chemistry*, 2nd Edition, p. 1042, J. Wiley & Sons, New York 1943.

⁷⁴ R. P. LINSTEAD and E. G. NOBLE, *J. Chem. Soc.* **1934**, 614.

⁷⁵ A. A. GOLDBERG and R. P. LINSTEAD, *J. Chem. Soc.* **1928**, 2343.

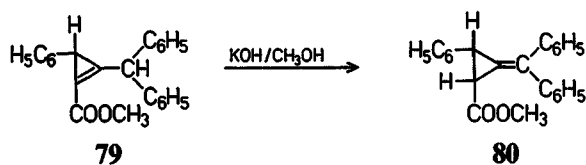
⁷⁶ G. A. R. KON, R. P. LINSTEAD, and G. W. G. MACLENNAN, *J. Chem. Soc.* **1932**, 2454.

⁷⁷ R. P. LINSTEAD, *J. Chem. Soc.* **1929**, 2498.

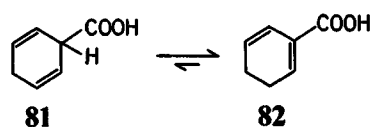
⁷⁸ R. A. LETCH and R. P. LINSTEAD, *J. Chem. Soc.* **1932**, 443.

⁷⁹ M. NAUDET L. COMEAU, and J. PASERO, *Rev. Franç. Corps Gras* **12**, 175 (1965); *C. A.* **63**, 485 (1965). see also paragraph 3. of this review and the literature references cited there.

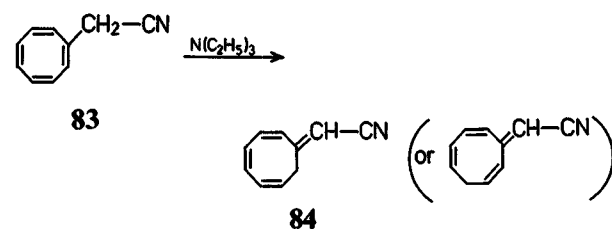
80 by treatment with methanolic potassium hydroxide solution⁸²:



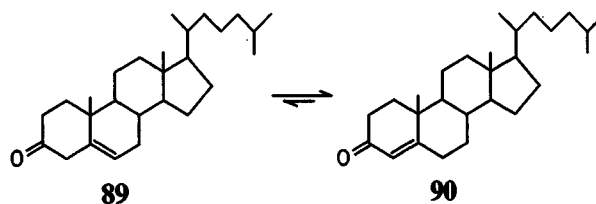
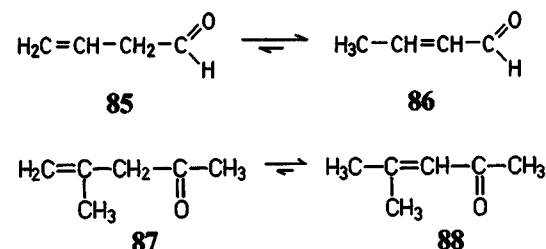
Double-bond shift in cyclohexa-2,5-dienecarboxylic acid (**81**) to give the more stable cyclohexa-1,5-dienecarboxylic acid (**82**) occurs slowly without catalyst at room temperature; it is accelerated by treatment with aqueous potassium hydroxide solution at reflux temperature⁸³:



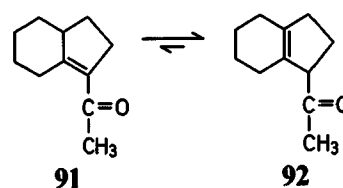
In the case of the nitrile of cyclooctatetraenylacetic acid (**83**), the isomer containing an exocyclic double bond is the more stable; upon heating at reflux temperature in triethylamine as solvent, **83** is converted to cyclooctatrienylideneacetic acid nitrile (**84**) in 87% yield⁸⁴:



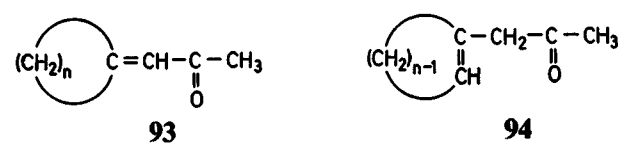
The rules applicable to the isomerization of unsaturated acids and their derivatives also apply in general to unsaturated aldehydes and ketones. Thus, Δ^3 -butenal (**85**)⁸⁵, 4-oxo-2-methyl-1-pentene (**87**)^{85,86}, and Δ^5 -cholestenone (**89**)⁸⁵ are less stable than their conjugated isomers **86**, **88**, and **90**, respectively, to which they can be converted using triethylamine⁸⁵, sodium hydroxide⁸⁶, or sodium methoxide⁸⁵ as catalyst in methanol:



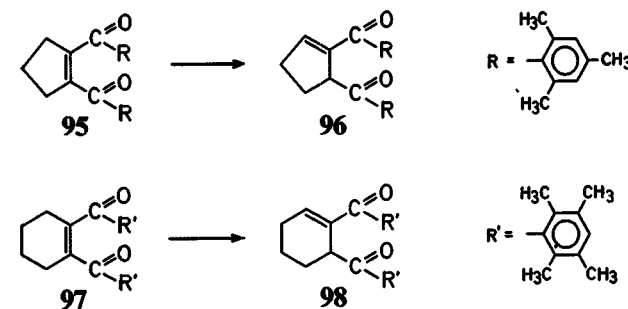
However, 1-acetyl- $\Delta^{3a,7a}$ -hexahydroindene (**92**) is more stable than its conjugated $\Delta^{1,7a}$ -isomer **91**; the equilibrium mixture obtained from **91** after treatment with sodium methoxide in methanol at room temperature for 48 hours⁸⁷ contains 80% of compound **92**:



If a carbonyl function is placed in the β -position of an alkyl side chain attached to an olefinic ring system, the conjugated exocyclic olefin (**93**) is thermodynamically more stable in the case of 5- and 7-membered rings ($n=4; 6$), and the non-conjugated endocyclic olefin (**94**) in the case of 6-membered rings ($n=5$)⁸⁸:



Interestingly, vicinal diarylcycloalkenes are most stable in the form of the isomers in which only one carbonyl group is conjugated with the olefinic double bond (**96**; **98**). This may be due to steric strains present in the isomer with the double bond between the two aroyl groups (**95**; **97**)⁸⁹. Using sodium hydroxide as catalyst in ethanol as solvent (24 hr at room temperature), compounds **95** and **97** may be converted to the isomers **96** and **98**, respectively, in 93% yield:



⁸⁰ R. T. HOLMAN and H. HAYES, *Anal. Chem.* **30**, 1422 (1958).
D. ARIGONI et al., *Experientia* **19**, 522 (1963).
see also: H. P. KAUFMANN and B. GROTHUES, *Fette, Seifen, Anstrichmittel* **61**, 425 (1959).

⁸¹ M. VERNY and R. VESSIERE, *Tetrahedron* **25**, 263 (1969).

⁸² N. A. AMPLOGOVA, I. A. DYAKONOV, and R. R. KOSTIKOV, *Zh. Org. Khim.* **2**, 1898 (1966); *C. A.* **66**, 55121 (1967).

⁸³ H. PLEININGER and G. EGE, *Chem. Ber.* **94**, 2088 (1961).

⁸⁴ A. C. COPE, R. M. PIKE, and D. F. RUGEN, *J. Amer. Chem. Soc.* **76**, 4945 (1954).

⁸⁵ H. C. VOLGER and W. BRACKMAN, *Rec. Trav. Chim.* **84**, 1017 (1965).

⁸⁶ F. H. STROSS, J. M. MONGER, and H. de V. FINCH, *J. Amer. Chem. Soc.* **69**, 1627 (1947).

Air must be excluded from these reaction mixtures, since the cyclopentene and cyclohexene derivatives are easily dehydrogenated to give fulvene derivatives or 1,2-diaroylbenzenes, respectively⁸⁹. As in many other cases, the tendency to isomerization of **95** and **97** has to be taken into account in the preparation of these compounds.

Shift of the olefinic double bond away from the 1,2-position in the compounds **95** and **97** appears to be a rather general phenomenon; on alkaline hydrolysis, the anhydrides and esters of some vicinal cyclohexadienedicarboxylic acids undergo a similar isomerization⁹⁰.

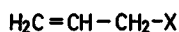
2.2. Isomerization of Olefins Containing Hetero Functions Other than Carbonyl or Cyano Groups

Hetero functions in the α -position or attached to the olefinic double bond are decisive in determining the position of the equilibrium between the isomers of an olefinic compound. The isomer possessing the vinyl structure is generally favored if it is stabilized by a substituent of the below listed type:



more stable when X = OR, SR, NR₂, P(O)R₂, PR₃, NO₂

In the case of substituents such as sulfone or ammonio groups, the allylic isomer generally is the more stable:

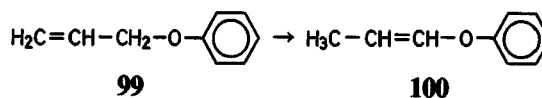


more stable when X = SO₂R, NR₃⁺

2.2.1. Isomerization of Olefins Containing Oxygen Functions

Base-catalyzed isomerization of allyl ethers may be used as a convenient method for the preparation of the corresponding propenyl ethers. The reaction is carried out using potassium t-butoxide as catalyst without solvent, or even better, in dimethyl sulfoxide as solvent⁹¹. Thus, allyl phenyl ether (**99**) affords

propenyl phenyl ether (**100**) in almost quantitative yield when treated with the above catalyst in dimethyl sulfoxide at 25°:



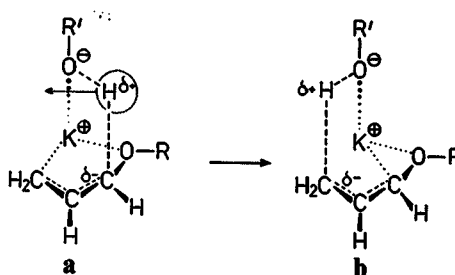
High stereospecificity is observed; compound **100** obtained from the reaction is 99% *cis*⁹¹. Under the above conditions, a 50% conversion is achieved within only 1.5 minutes.

1,2-Dimethoxyethane has also been used as solvent in the isomerization of allyl ethers⁹², although rates and stereospecificity are lower⁹¹.

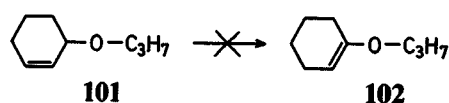
Typical examples of base-catalyzed isomerization of allyl ethers into the corresponding propenyl ethers, a reaction which has potential in preparative chemistry, are given below; potassium t-butoxide was employed as catalyst without solvent, and the reactions were performed in heavy-walled vials at 150–175° with a reaction time of 5 hours⁹² (initial allyl ether and yield of propenyl ether given):

Hexadecyl allyl ether	96%
1,4-Diallyloxybutane	99%
1,5-Diallyloxybutane	94%
Pentaerythritol triallyl ether	79%

The obvious predomination of *cisoid* propenyl ethers as products of the above mentioned isomerization has been explained, aside from their thermodynamic stability, by the postulation of two intermediates (**a** and **b**) possessing bridged hydrogen bonds. The labilized hydrogen atom in the C₁-position of intermediate **a** is transferred to the C₃-position, thus forming intermediate **b** which is then cleaved to give the *cis*-propenyl ether⁹¹:



The failure of 3-propyloxycyclohexene (**101**), which contains a *transoid* allyl ether group, to undergo base-catalyzed isomerization to **102** is in accordance with the postulated mechanism:



⁸⁷ W. L. MEYER and J. F. WOLFE, *J. Org. Chem.* **27**, 3263 (1962).

⁸⁸ A. H. DICKINS, W. E. HUGH, and G. A. R. KON, *J. Chem. Soc.* **1928**, 1630; **1929**, 572.
W. E. HUGH, G. A. R. KON, and T. MITCHELL, *J. Chem. Soc.* **1929**, 1435.
G. A. R. KON, *J. Chem. Soc.* **1930**, 1616.
For a discussion see: H. C. BROWN, J. H. BREWSTER, and H. SCHECHTER, *J. Amer. Chem. Soc.* **76**, 468 (1954).

⁸⁹ R. C. FUSON and J. A. HAEFNER, *J. Org. Chem.* **27**, 1957 (1962).

⁹⁰ V. F. KUCHEROV and N. Y. GRIGOREVA, *Doklady Akad. Nauk SSSR* **128**, 547 (1959); *C. A.* **60**, 7583 (1960).

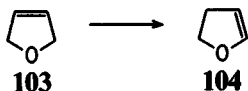
⁹¹ C. S. PRICE and W. H. SNYDER, *J. Amer. Chem. Soc.* **83**, 1773 (1961).

⁹² T. J. PROSSER, *J. Amer. Chem. Soc.* **83**, 1701 (1961).

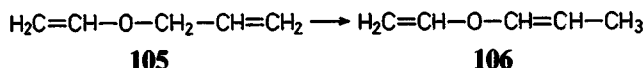
⁹³ R. PAUL, M. FLUCHAIRE, and G. COLLARDEAU, *Bull. Soc. Chim. France* **1950**, 668.

⁹⁴ R. PAUL, G. ROY, M. FLUCHAIRE, and G. COLLARDEAU, *Bull. Soc. Chim. France* **1950**, 121.
see also: D. M. SIMONS and J. VERBANC, *J. Polymer. Sci.* **44**, 303 (1960); isomerization of allyl ethers in the presence of aqueous sodium hydroxide.

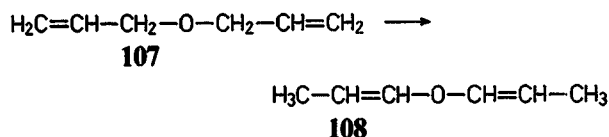
2,5-Dihydrofuran (**103**), which is capable of forming a *cis*-allylic intermediate of type a, however, is readily converted to 4,5-dihydrofuran (**104**; 93%) by treatment (7 hr) with potassium *t*-butoxide or potassium hydroxide in *t*-butanol at 185–190°:



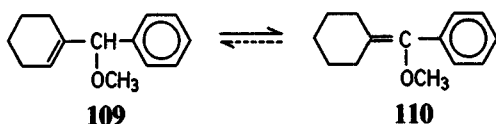
Vinyl allyl ether (**105**) is isomerized to vinyl propenyl ether (**106**) in good yield under the same conditions⁹⁴:



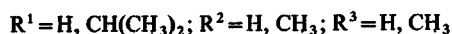
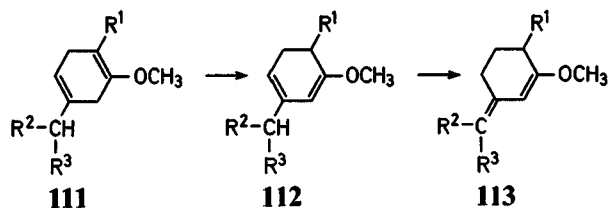
Similarly, bis-[1,3-diphenylallyl]ether is converted to bis-[1,3-diphenylpropenyl]ether⁹⁵. Isomerization of diallyl ether (**107**) to dipropenyl ether (**108**) has been carried out using a sodium-on-alumina catalyst activated by ferric oxide³¹:



The equilibrium obtained upon heating either one of the isomeric ethers **109** or **110** at 100° (20 hr) in dimethyl sulfoxide in the presence of potassium *t*-butoxide⁹⁶ lies in favor of the exocyclic (vinylic) isomer **110**:



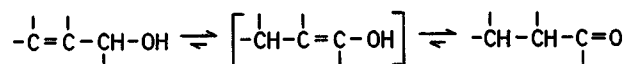
In the six-membered cyclic olefins, the endocyclic isomers are generally more stable than the exocyclic (see paragraph 1.3). This is, however, not necessarily the case if the exocyclic isomer may be stabilized by conjugation. For example, in the base-catalyzed isomerization of some 1-methoxy-5-alkylcyclohexa-1,4-dienes (**111**) using sodium amide in liquid ammonia⁹⁷, it was shown that the exocyclic isomer (**113**) formed by a stepwise hydrogen shift (**111** → **112** → **113**) is the most stable except in the case of $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{CH}_3$. In the latter case, only the endocyclic isomer **112** is obtained:



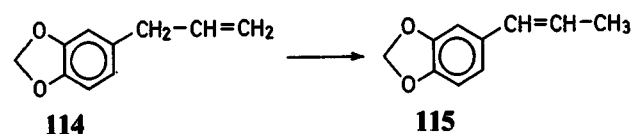
Under the influence of strong bases such as phenyllithium or sodium amide in polar or aprotic solvents,

allyl ethers rearrange to yield alcohols⁹⁸ or carbonyl derivatives⁹⁹ (Wittig rearrangement). This reaction will not be discussed here.

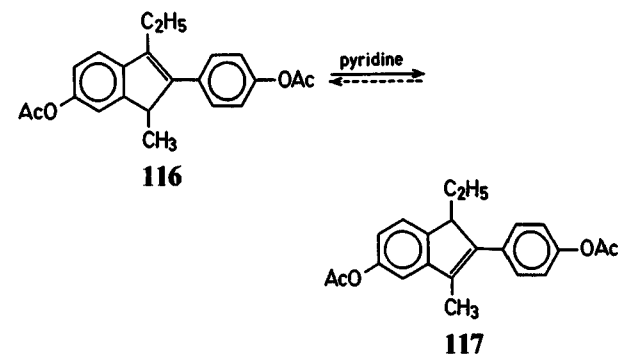
Allyl alcohols undergo the same type of double-bond isomerization as allyl ethers; however, the products isolated are the carbonyl derivatives produced by tautomerism of the vinyl alcohols (enols) initially formed:



Safrol (3,4-methylenedioxy-1-allylbenzene; **114**) has been isomerized to the propenyl isomer **115** using a sodium-on-alumina catalyst activated with ferric oxide³¹:



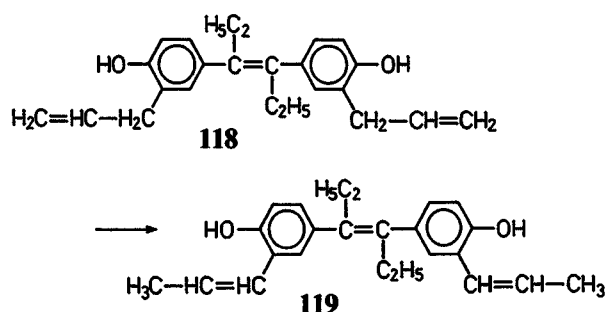
In the indene series, isomerization of the diacetoxy derivative **116** to give compound **117** in 74% yield has been accomplished by heating in pyridine solution at 100° for 4.5 hours¹⁰⁰:



Isomerization of allylphenols to the corresponding propenyl derivatives may be carried out in aqueous potassium hydroxide solution containing aniline¹⁰¹, in aqueous diethylene glycol¹⁰², or in butanol¹⁰³, in each case at temperatures above 100°. Thus,

- ⁹⁵ C. W. SHOPPER, *J. Chem. Soc.* **1928**, 2567.
S. PATAI, *The Chemistry of Alkenes*, p. 423, Interscience Publishers, London · New York · Sidney 1964.
- ⁹⁶ I. ELPHIMOFF-FELKIN and J. HUET, *Tetrahedron Letters* **1966**, 1933.
- ⁹⁷ A. J. BIRCH, E. M. A. SHOUKRY, and F. STANSFIELD, *J. Chem. Soc.* **1961**, 5376.
- ⁹⁸ G. WITTIG and L. LÖHMANN, *Liebigs Ann. Chem.* **550**, 260 (1942).
C. R. HAUSER and S. W. KANTOR, *J. Amer. Chem. Soc.* **73**, 1437, 4122 (1951).
- ⁹⁹ J. CAST, T. S. STEVENS, and J. HOLMES, *J. Chem. Soc.* **1960**, 3521.
M. SCHLOSSER, *J. Organometal. Chem.* **8**, 9 (1967).
- ¹⁰⁰ H. FELKIN and A. TAMBUTÉ, *Tetrahedron Letters* **1969**, 821.
- ¹⁰¹ E. ADLER and B. HÄGGLUND, *Arkiv för Kemi [A]* **19**, No. 23 (1945); *C. A.* **41**, 2030 (1947).

3,4-bis-[4-hydroxy-3-allylphenyl]-hexene (**118**), a derivative¹⁰² of stilbestrol, was converted to the propenyl isomer **119**:



2.2.2. Isomerization of Olefins Containing Sulfur Functions

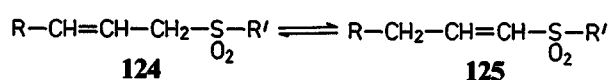
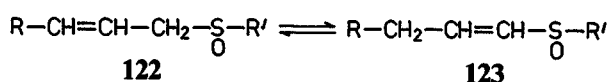
Among the unsaturated thioethers, the vinylic isomers (**121**) usually are more stable than the allylic isomers (**120**); equilibration is readily achieved using basic catalysts such as aqueous sodium hydroxide¹⁰⁴, sodium ethoxide in ethanol¹⁰⁵, or (better) potassium *t*-butoxide in 1,2-dimethoxyethane¹⁰⁶ or dimethyl sulfoxide¹⁰⁷:



Thus, treatment of hexyl allyl sulfide (**120**, R = H, R' = C₆H₁₃) with sodium ethoxide in ethanol as solvent at reflux temperature (12 hr) yields hexyl propenyl sulfide in 61% yield¹⁰⁵. Almost complete isomerization of diallyl sulfide to dipropenyl sulfide is accomplished with potassium *t*-butoxide in 1,2-dimethoxyethane (exothermic reaction) or sodium *t*-butoxide in the same solvent at room temperature¹⁰⁶.

The percentage of *trans* isomer in the isomerization product has been found to be higher than in the analogous isomerization of allyl ethers. For example, 1-methylmercapto-1-hexene, upon treatment with potassium *t*-butoxide in dimethyl sulfoxide gives rise to 29% *cis*- α,β -, 38% *trans*- α,β -, and 33% β,γ -unsaturated sulfide¹⁰⁷.

In contrast to the case of thioethers, the equilibria of unsaturated sulfoxides and of open-chain unsaturated sulfones^{107,108} possessing at least four carbon atoms in the olefin residue, favor the allylic isomers (**123** and **125**):



¹⁰¹ U.S. Patent 2516412 (1950), Sulphite Products Corp., I.A. PEARL; C.A. 44, 10736 (1950).

¹⁰² E. KAISER and J.J. SVARZ, J. Amer. Chem. Soc. 68, 636 (1946).

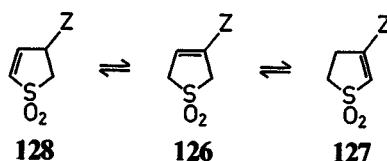
This fact has been explained in terms of low resonance between the olefinic double bond and the sulfoxide or sulfone group and of the electron withdrawing properties ($-I$ effect) of these groups^{107,108} which destabilize the α,β -double bond.

However, alkyl-substitution in the γ -position of the allyl group is also decisive in controlling the position of equilibrium. Allyl sulfoxides and sulfones with R = H are less stable than their propenyl isomers. Thus, starting with either methyl allyl sulfoxide or methyl propenyl sulfoxide and using potassium *t*-butoxide in *t*-butanol at reflux temperature (18 hr), an equilibrium mixture is obtained which consists of 20% allyl isomer (**122**, R = H, R' = CH₃) and 80% propenyl isomer (**123**)¹⁰⁷. On the other hand, equilibration of, for instance, 1-methylsulfinio-1-hexene (**123**, R = C₃H₇, R' = CH₃) using the same catalyst produces an equilibrium mixture which contains 94% of the corresponding allylic isomer **122**.

In the sulfone series, equilibration of the 2-undecene derivative **125** (R = C₈H₁₇, R' = CH₃) even yields 99% of the allylic isomer **124**. With methyl propenyl sulfone as starting material (**125**, R = H, R' = CH₃), an equilibrium mixture containing 44% allyl (**124**) and 56% propenyl isomer (**125**) is obtained¹⁰⁷.

Aryl and benzyl allyl sulfones have also been converted to their propenyl isomers by alkaline isomerization¹⁰⁹.

In the case of unsaturated cyclic sulfones, the position of equilibrium depends upon the ring size and the substituents. With either one of the isomeric dihydrothiophene-1,1-dioxides as starting material (**126** and **127**, Z = H), an equilibrium mixture containing 41% of the allylic isomer (**126**) and 59% of the vinylic isomer (**127**) is obtained¹¹⁰ upon treatment with aqueous sodium hydroxide at 50°:



If Z = OCH₃, the equilibrium is almost completely shifted in favor of 3-methoxy-4,5-dihydrothiophene-1,1-dioxide (**127**)¹¹¹. A similar shift of the equilibrium has been observed¹¹² in the alkaline isomerization of the 3-methyl derivative (91% of **127**, R = CH₃).

¹⁰³ E. KAISER, E. DOMBA, and M. SKIBBE, J. Org. Chem. 27, 2931 (1962).

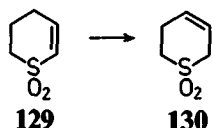
¹⁰⁴ D.S. TARBELL and M.A. MCCALL, J. Amer. Chem. Soc. 74, 48 (1952).

¹⁰⁵ D.S. TARBELL and W.E. LOVETT, J. Amer. Chem. Soc. 78, 2259 (1956).

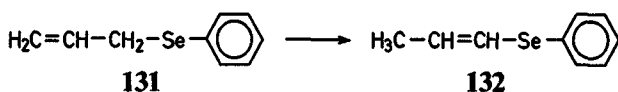
¹⁰⁶ C.C. PRICE and W.H. SNYDER, J. Org. Chem. 27, 4639 (1962).

¹⁰⁷ D.E. O'CONNOR and W.I. LYNES, J. Amer. Chem. Soc. 86, 3840 (1964).

The base-catalyzed isomerization of dihydro-4H-thiapyran-1,1-dioxide (129) appears to be an irreversible reaction; the allylic isomer 130 is obtained in high yield and only 3% of compound 129 are present in the resultant reaction mixture^{108,113}:

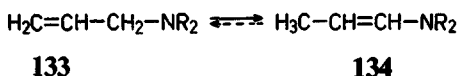


Analogous to methyl and aryl allyl sulfides, phenyl allyl selenide (131) undergoes isomerization in the presence of potassium t-butoxide in t-butanol to afford phenyl propenyl selenide (132) in almost quantitative yield¹¹⁴:



2.2.3. Isomerization of Olefins Containing Nitrogen Functions

Allyl amines (133) may be readily isomerized to enamines (134) using basic catalysts such as potassium t-butoxide or potassium amide:



cis-Enamines are initially formed, but subsequent isomerization to the usually more stable *trans*-isomers occurs readily^{115,116}. Thus, diethyl allyl amine is converted to diethyl *cis*-propenyl amine (90%) by treatment with potassium t-butoxide in anhydrous dimethyl sulfoxide (90 hr) at 20° in a nitrogen atmosphere¹¹⁵. Upon further standing, the *trans*-isomer is formed; this isomerization is catalyzed by traces of carbon dioxide, benzoic acid, or alcohols.

The heterogeneous catalysis by potassium amide on alumina of the isomerization of allyl amines into enamines is particularly useful because of the ease of isolation of the isomerized product¹¹⁷.

¹⁰⁸ D. E. O'CONNOR and W. I. LYNESS, *J. Amer. Chem. Soc.* **85**, 3044 (1963).

Belg. Patent 669122 (1966), Procter & Gamble Co., W. I. LYNESS and D. E. O'CONNOR; *C. A.* **65**, 16866 (1966).

K. MUZIKA, M. PROCHÁZKA, and M. PALIČEK, *Collection Czech. Chem. Commun.* **34**, 635 (1969).

¹⁰⁹ H. J. BACKER and G. J. DEJONG, *Rec. Trav. Chim.* **67**, 884 (1948).

H. J. BACKER, J. STRATING, and J. DRENTH, *Rec. Trav. Chim.* **70**, 365 (1951).

¹¹⁰ C. D. BROADUS, *J. Amer. Chem. Soc.* **88**, 3865 (1966).

¹¹¹ M. PROCHÁZKA and M. PALIČEK, *Collection Czech. Chem. Commun.* **31**, 3744 (1966).

¹¹² J. BOESEKEN and E. DE ROY VAN ZUYDEWIJN, *Proc. Acad. Sci. (Amsterdam)* **40**, 23 (1937); *C. A.* **31**, 4953 (1937).

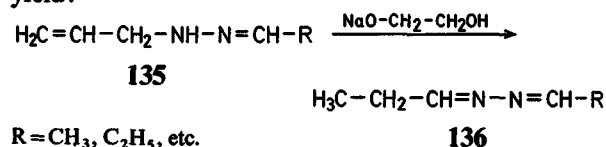
L. K. BRICE, W. M. CHANG, J. E. SMITH, and S. M. SULLIVAN, *J. Phys. Chem.* **71**, 2814 (1967).

Isomerization of allyl amines¹¹⁷: Ammonia (~30 ml) is condensed into an Erlenmeyer flask cooled in Dry-Ice/acetone and fitted with a drying tube. Alumina (20 g) is added, followed by potassium (1.2 g), and a crystal of ferric nitrate. The ammonia is evaporated by stirring the mixture at room temperature under a nitrogen atmosphere. As soon as the ammonia is removed, a solution of the allylamine (e.g. N,N-diethyl allylamine) (15–45 g) in pentane (25–75 ml) is quickly poured over the catalyst. The reaction is followed by i.r. spectroscopy: the vinyl group absorptions at 10.06 and 10.94 μ disappear slowly and the reaction is stopped when this process is complete (generally less than 30 min.). The catalyst is removed by filtration, the solvent distilled under reduced pressure, and the residue fractionally distilled in vacuo. The i.r. spectrum exhibits typical enamine absorption at 6.03 μ . The yield of pure material isolated is about 70% in most cases.

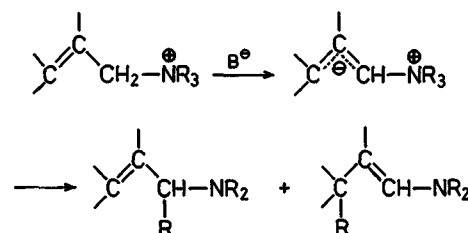
Dialkylallylamines, N-allylpyrrolidine, N-allylpipe-ridine, N-allylmorpholine, and N-allylcarbazole have been isomerized to the corresponding propenyl derivatives by this technique.

The isomerization of alkylallylamines has also been carried out in the gas phase at 260–270° using potassium hydroxide on alumina as catalyst¹¹⁸; the isomeric propenylamines are the major products (26–50%); propylideneamines are obtained as side products (10–15%).

Base-catalyzed isomerization of the allylhydrazones of aldehydes and ketones gives rise to azines¹¹⁹. Thus, acetaldehyde and propanal allylhydrazone (135) upon treatment with the monosodium derivative of glycol in glycol as solvent give acetaldehyde propanal azine or propanal azine (136), respectively, in 70% yield:



The base-catalyzed rearrangement of allylic quaternary ammonium salts (Stevens rearrangement)^{4,120} which involves migration of an alkyl group¹²¹



will not be discussed here.

¹¹³ E. A. FEHNEL and P. A. LACKEY, *J. Amer. Chem. Soc.* **73**, 2473 (1951).

E. A. FEHNEL, *J. Amer. Chem. Soc.* **74**, 1569 (1952).

¹¹⁴ E. G. KATAEV, L. M. KATAEVA, and G. A. CHMUTOVA, *Zh. Org. Khim.* **2**, 2244 (1966).

¹¹⁵ C. C. PRICE and W. H. SNYDER, *Tetrahedron Letters* **1962**, 69.

M. RIVIÈRE and A. LATTES, *Bull. Soc. Chim. France* **1967**, 2539; sodium amide in liquid ammonia was used as catalyst.

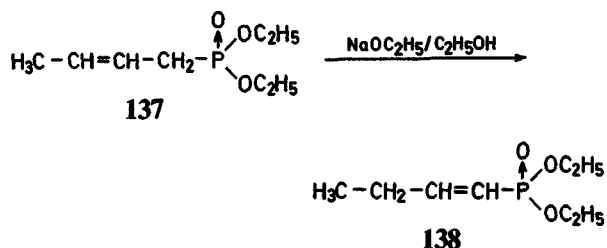
P. CAUBERE and M. F. HOCHU, *Bull. Soc. Chim. France* **1968**, 459.

M. RIVIÈRE and A. LATTES, *Bull. Soc. Chim. France* **1968**, 4430.

A study of the isomerization of an allylic nitro olefin lead to the conclusion that the isomer in which the double bond is conjugated with the nitro group is the more stable¹²².

2.2.4. Isomerization of Olefins Containing Phosphorus Functions

Sodium ethoxide in ethanol or potassium hydroxide in methanol catalyze the isomerization of diethyl Δ^2 -butenephosphonate (137),



diallylphenylphosphine oxide, Δ^2 -propene-benzephosphinic acid, Δ^2 -propenephosphonic acid, and diallylphenylphosphine to the corresponding propenyl derivatives (e.g. diethyl Δ^2 -phosphinate, 138)¹²³. Allylphosphonium salts have been isomerized analogously¹²⁴.

3. Isomerization of Olefins in Industrial Processes

A few examples may serve to demonstrate the importance of base-catalyzed isomerizations in industrial processes.

While the oxidation of a terminal olefin yields a carboxylic acid and formic acid (which is further oxidized to water and carbon dioxide), the oxidative cleavage of non-terminal olefins gives rise to two carboxylic acids (or, if the olefin is symmetrical about the double bond, two moles of one carboxylic acid). Base-catalyzed isomerisation of terminal olefins

may be used to obtain the more valuable isomers possessing an internal double bond, the further reaction of which leads to the production of organic intermediates or final products.

In the petrochemical industry, olefin isomers containing a non-terminal double bond are valuable because of their high octane number¹²⁶.

The drying properties of unsaturated fatty acids containing two or more isolated double bonds (e.g. linoleic and linolenic acid) may be improved by base-catalyzed isomerization into the conjugated isomers¹²⁷. The isomerization is also performed with unsaturated alcohols and esters (e.g. linolenol, methyl linolenate, linseed and soybean oils, C_6 — C_{24} polyenic alcohols)¹²⁸.

Moreover, the base-catalyzed isomerization of some highly unsaturated polymeric hydrocarbons in aprotic solvents affords products which possess excellent cure properties and which are utilized as coating materials, adhesives, and so forth¹²⁹.

¹¹⁶ J. SAUER and H. PRAHL, *Tetrahedron Letters* **1966**, 2863.

¹¹⁷ A. J. HUBERT, *J. Chem. Soc. [C]* **1968**, 2048.

¹¹⁸ G. Y. KONDRATEVA and Y. S. DOLSKAYA, *Izv. Akad. Nauk SSSR, Ser. Khim.* **1967**, 2045; *C.A.* **68**, 19202 (1968).

¹¹⁹ B. V. IOFFE and A. P. KOTSCHETOV, *Tetrahedron Letters* **1968**, 1329.

B. V. IOFFE and V. S. STOPSKI, *Tetrahedron Letters* **1968**, 1333.

¹²⁰ T. S. STEVENS, E. M. CREIGHTON, A. B. GORDON, and M. MACNICOL, *J. Chem. Soc.* **1928**, 3193.

T. THOMSON and T. STEVENS, *J. Chem. Soc.* **1932**, 55.

J. L. DUNN and T. S. STEVENS, *J. Chem. Soc.* **1934**, 279.

¹²¹ For a discussion of the mechanism of the Stevens rearrangement see: E. F. JENNY and J. DRUEY, *Angew. Chem.* **74**, 152 (1962).

H. HELLMANN and G. M. SCHEFFT, *Liebigs Ann. Chem.* **654**, 39 (1962).

¹²² H. SHECHTER and J. W. SHEPHERD, *J. Amer. Chem. Soc.* **76**, 3617 (1954).

¹²³ J. H. DAVIES and P. KIRBY, *J. Chem. Soc.* **1964**, 3425.

¹²⁴ P. T. KEOUGH and M. GRAYSON, *J. Org. Chem.* **29**, 631 (1964).

¹²⁵ F. ASINGER and B. FELL, *Erdöl und Kohle* **19**, 345 (1966).

¹²⁶ F. A. FIDLER, *The Science of Petroleum*, V, Part I, p. 107, Oxford University Press 1966.

¹²⁷ M. NAUDET, L. COMEAU, and J. PARERO, *Rev. Franç. Corps Gras* **12**, 175 (1965).

M. L. SWAIN and B. A. BRICE, *J. Amer. Oil Chemist's Soc.* **26**, 272 (1949).

K. FOSSAN, *Tidsskrift for Kjemi, Bergvesen og Metallurgi* **7**, 12 (1947).

A. M. ABU-NASR and R. T. HOLMAN, *J. Amer. Oil Chemist's Soc.* **32**, 414 (1955).

¹²⁸ K. FUKUZUMI and T. MIGAKAWA, *Kogyo Kagaku Zasshi* **67**, 2065 (1964); *C.A.* **63**, 2006 (1965).

R. V. CRAWFORD, *Paint, Oil, Colour J.* **149**, 3510 (1966).

K. L. MIKOLAJCZAK, M. O. BAGBY, and I. A. WOLFF, *J. Amer. Oil Chemist's Soc.* **42**, 243 (1965); *C.A.* **63**, 6850 (1965).

L. DAVENPORT, *Chem. & Ind.* **1956**, 136.

T. AKIYA, *Shokweyo Kenkyusho Kenkyu Hokoku* **12**, 73 (1957); *C.A.* **57**, 12863 (1962).

German Patent 1196645 (1965), Henkel & Cie., W. STEIN, G. WALTHER; *C.A.* **63**, 11359 (1965).

S. MASUYAMA, *Nippon Nōgei-Kagaku Zasshi* **28**, 383 (1954); *C.A.* **51**, 10089 (1957).

A. BHATI, *Perfumery and Essential Oil Record* **54**, 448 (1963); *C.A.* **63**, 13322 (1965).

¹²⁹ U.S. Patent 3281487 (1966), Esso Research and Engineering Co., C. A. ROWE, A. SCHRIESHEIM, D. L. BAEDER; *C.A.* **66**, 11927 (1967).

¹³⁰ L. REGGEL, C. ZAHN, I. WENDER, and R. RAYMOND, *U.S. Bur. Mines, Bull.* **1965**, (615), 4.

¹³¹ French Patent 1363842 (1964), M. AMAGASA, T. YAMAGUCHI; *C.A.* **61**, 9414 (1964).

¹³² Jap. Patent 10137/65, 10138/65, T. YAMAGUCHI, M. TANAKA; *C.A.* **63**, 5540 (1965).

¹³³ I. V. GOTUNSKAYA, N. I. TYUNKINA, and B. A. KAZANSKII, *Doklady Akad. Nauk SSSR* **108**, 473 (1956).

I. V. GOTUNSKAYA, N. B. DOBROSERDOVA, M. R. BERDNIKOVA, and B. A. KAZANSKII, *Kinetika i Kataliz* **1**, 612 (1960).

¹³⁴ U.S. Patent 2965689 (1960), Standard Oil Co. (Indiana), A. K. ROEBUCK, B. L. EVERING; *C.A.* **55**, 25234 (1961).

¹³⁵ Brit. Patent 990465 (1965), British Petroleum Co., J. K. HAMLING, G. W. ALDERSON; *C.A.* **63**, 4161 (1965).

¹³⁶ U.S. Patent 3201493 (1965), E. E. MEISINGER, H. S. BLOCH; *C.A.* **63**, 13072 (1965).

A great number of patents claim the use of a basic catalyst for olefin isomerization^{125,126}. Alkali metal hydroxides and methoxides are used in the isomerization of unsaturated acids^{127,128}. Other catalysts employed in commercial processes are lithium in ethylene diamine¹³⁰, sodium¹³¹ or sodium ethoxide¹³² in liquid ammonia, calcium amide¹³³,

sodium on alumina or active charcoal¹³⁴, and potassium¹³⁵ or potassium amide¹³⁶ on alumina. However, in recent years processes using transition metal catalysts have received much study (see Part II of this review).

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