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Prototropic Isomerisation of Olefins with Functional Groups and Its Use in Organic Synthesis

L.A.Yanovskaya and Kh.Shakhidayatov

The characteristics and mechanism of the prototropic isomerisation of olefins with functional groups in the presence of bases, acids, metal carbonyls, and other catalysts and also by thermal and photochemical activation have been examined together with its application in organic synthesis.
The bibliography includes 180 references.

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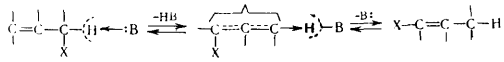
I. INTRODUCTION

In recent years there has been a considerable growth of interest in the problem of the migration of double bonds in olefins with functional groups. A number of new effective isomerisation catalysts have been proposed and novel methods of synthesis based on prototropic isomerisation have been developed. This review gives a general account of the advances in the study of the mechanism and use in syntheses of the prototropic shift in olefins with functional groups achieved in the last 10–15 years.

A brief review of the literature on this problem up to 1960–1961 is given in "The Chemistry of Alkenes",[1] but it does not deal at all with isomerisation in the presence of metal carbonyls and with thermal and photochemical isomerisation. Information about base-catalysed isomerisation of olefins including some with functional groups is given in the review by Hubert and Reimlinger[2].

II. ISOMERISATION IN THE PRESENCE OF BASES

The prototropic shift under the influence of bases in olefins with functional groups takes place by a carbanionic mechanism[3,4]:



The reaction is reversible. The position of equilibrium depends on the structure of the olefin and the nature of the functional group X, as shown already in the classical work of Kon and Linstead[2,3] on the prototropic isomerisation of unsaturated acids, their esters, and nitriles, and confirmed in subsequent investigations.

For the system $CH_2{=}CHCH_2X{\rightleftharpoons}CH_3CH{=}CHX$, where X may be conjugated with an $\alpha\beta$-double bond via an unshared electron pair (X = OR, SR, NR_2, etc.) or π electrons (X = COOH, COOR, CN, CHO, COR, etc.), the equilibrium is usually displaced towards the conjugated system. For example, alkyl allyl[5], allyl aryl[6], and allyl vinyl[7] ethers are almost completely converted into propenyl ethers on heating with potassium t-butoxide. Similarly, under the influence of alkoxides and other bases, alkyl allyl sulphides[8] and allyl aryl sulphides[9] form equilibrium mixtures where the ratio of the propenyl and allyl forms is 99:1. Allyl phenyl selenide isomerises quantitatively to phenyl propenyl selenide in the presence of potassium t-butoxide[10]. The isomerisation of *NN*-disubstituted allylamines[11–13] to enamines goes to completion in the presence of bases and in most cases the equilibrium constants cannot be determined. Under the action of alkalis, vinylacetic acid is converted into an equilibrium mixture containing 98% of crotonic acid[14]. The equilibrium in mixtures of vinylacetonitrile with crotononitrile or of ethyl vinylacetate with ethyl crotonate is also almost completely displaced towards the $\alpha\beta$-isomer[15].

If the group X is incapable of conjugation with the $\alpha\beta$-double bond (X = SO, SO_2, etc.), then the equilibrium mixture contains an appreciable amount of the $\beta\gamma$-isomer. Thus the equilibrium mixture of allyl methyl sulphoxide and methyl propenyl sulphoxide contains 17–20% of the $\beta\gamma$-isomer[16] and a mixture of allyl methyl sulphone and methyl propenyl sulphone contains 44% of the $\beta\gamma$-isomer[17]. The equilibrium position in alkyl cycloalkyl sulphones[18] and in cyclic sulphones[18,19] is likewise shifted towards the $\beta\gamma$-isomer.

Substitution (in the first place in the γ-position) in a three-carbon system has an enormous influence on the equilibrium position (Table 1). Table 1 shows that substituents in the γ-position displace the equilibrium towards the $\beta\gamma$-isomer, which may actually predominate. For alkyl groups, this can be explained by the competition between the effect of the conjugation of the functional groups with the double bond, which stabilises the $\alpha\beta$-form, and the effect of the hyperconjugation of the alkyl group with the double bond, which stabilises the $\beta\gamma$-form. If the latter effect prevails, then the $\beta\gamma$-isomer predominates in the equilibrium mixture. The decrease of the hyperconjugation effect in the sequence $H<(CH_3>C_2H_5>iso\text{-}C_3H_7>t\text{-}C_4H_9)$ results in a somewhat smaller effect of higher alkyl groups on the equilibrium position. An alkyl group in the α-position additionally stabilises the $\alpha\beta$-isomer owing to hyperconjugation and therefore the $\alpha\beta$-isomer predominates in the equilibrium mixture even

in the presence of a substituent in the γ-position. In $\beta\gamma$-disubstituted derivatives the content of the $\alpha\beta$-form is also somewhat increased. The presence of a substituent in the α- or β-position only has hardly any influence on the equilibrium. Thus mesityl oxide contains only 1.3% of the $\beta\gamma$-form [22,23].

Table 1. Equilibrium positions in certain three-carbon systems.

$\alpha\beta$-Isomer	%	$\beta\gamma$-Isomer	%	References
$C_6H_5CH_2CH{=}C(CH_3)OCH_3$	90	$C_6H_5CH{=}CHCH(CH_3)OCH_3$	10	20
$RCH_2CH{=}CHSCH_3$		$RCH{=}CHCH_2SCH_3$		17
R=H	67	R=H	33	
R=n-C_3H_7	66	R=n-C_3H_7	34	
RR'CHCR''=CR'''COOH		RR'C=CR''CH R'''COOH		21
R=R'=R''=R'''=H	98	R=R'=R''=R'''=H	2	
R=CH_3, R'=R''=R'''=H	68	R=C_2H_5, R'=R''=R'''=H	32	
R'=C_2H_5, R'=R''=R'''=H	74	R=C_2H_5, R'=R''=R'''=H	28	
R=R'=CH_3, R''=R'''=H	6	R=R'=CH_3, R''=R'''=H	94	
R=R''=CH_2, R'=R''=H	81	R=R'''=CH_3, R'=R''=H	19	
R=CH_3, R'=R''=H, R'''=C_2H_5	21	R=CH_3, R'=R'''=H, R''=C_2H_5	79	
R=C_2H_5, R'=R''=H, R'''=H= n-C_3H_7	34	R=C_2H_5, R'=R'''=H, R''= n-C_3H_7	66	
$RCH_2CH{=}CHS(O)CH_3$		$RCH{=}CHCH_2S(O)CH_3$		16, 17
R=H	80	R=H	20	
R=CH_3	3	R=CH_3	97	
R=n-C_6H_{13}	4	R=n-C_6H_{13}	96	

The stabilisation of the $\beta\gamma$-isomer by hyperconjugation has been confirmed by a number of investigations. Thus in the system n-$C_4H_9C(R){=}CHCH(CH_3)COOC_2H_5 \rightleftharpoons$ $\rightleftharpoons$n-$C_4H_9CH(R)CH{=}C(CH_3)COOC_2H_5$ the fraction of the $\alpha\beta$-isomer in the equilibrium mixture increases from 45 to 86% on passing from R = CH_3 to R = t-C_4H_9, in agreement with the decrease of the hyperconjugation effect [21]. Analogous results were obtained for ethyl *trans*-2-methyl-4-*p*-R-phenylbutenoates, where the effect of steric factors is excluded and there is no *cis–trans* isomerisation during the attainment of equilibrium [24] (Table 2).

Table 2. *p*-$RC_6H_4CH{=}CHCH(CH_3)COOC_2H_5 \rightleftharpoons$ *p*-$RC_6H_4CH_2CH{=}C(CH_3)COOC_2H_5$.

R	$\alpha\beta$-Isomer, %	$\beta\gamma$-Isomer, %	R	$\alpha\beta$-Isomer, %	$\beta\gamma$-Isomer, %
H	59.2	40.8	iso-C_3H_7	50	50
CH_3	39.8	60.2	t-C_4H_9	52.4	47.6
C_2H_5	45.9	54.1			

In the equilibrium mixture $C_6H_5CH_2SO_2CH{=}CHSO_2R \rightleftharpoons$ $\rightleftharpoons C_6H_5CH_2SO_2CH{=}CH{-}CH_2SO_2R$ the content of the first isomer also depends on the inductive effect of R, increasing in the series C_2H_5 (39%) < n-C_3H_7 (40%) < n-C_4H_9 (53%) < < t-C_4H_9 (60%). [25] The hyperconjugation effect accounts for the shift of equilibrium towards the second sulphone in the system $(C_2H_5)_2NO_2SCH{=}CHCH(CH_3)SO_2N(C_2H_5)_2 \rightleftharpoons (C_2H_5)_2N{-}$ $O_2SCH_2CH{=}C(CH_3)SO_2N(C_2H_5)_2$. [26]

Apart from the conjugation and hyperconjugation effects, the inductive effect of the functional group plays a major role in the stabilisation of the $\alpha\beta$- and $\beta\gamma$-forms. This is evident from a comparison of the equilibrium constants K for mixtures of certain unsaturated sulphides, sulphoxides, and sulphones [8] (Table 3).

Table 3 shows that the stability of the $\alpha\beta$-form decreases in a series $SO_2R > SOR > SR$, i.e. in order of increasing inductive effects. It should be borne in mind that in the system $RCH_2{-}CH{=}CHX \rightleftharpoons RCH{=}CHCH_2X$ the effect of the substituent X is greater than that of CH_2X.

Table 3. Equilibrium constants for mixtures of certain unsaturated sulphides, sulphoxides, and sulphones $RCH_2CH{=}CHX \rightleftharpoons RCH{=}CHCH_2X$.

R	X	K	R	X	K
H	SCH_3	0.01	n-C_9H_{19}	SO_2CH_3	99.0
H	$SOCH_3$	0.2–0.25	n-C_9H_{19}	SCH_3	0.5
H	SO_2CH_3	0.78	n-C_9H_{19}	$SOCH_3$	24.0
n-C_3H_7	SCH_3	0.51	n-C_9H_{19}	SO_2CH_3	24.0
n-C_3H_7	$SOCH_3$	24.0			

Electron-accepting substituents increased the mobility of the α-hydrogen atom in $RCH{=}CHCH_2X$ and favour the prototropic shift in accordance with the magnitude of the $-I$ effect. However, such substituents at the double bond destabilise the $\alpha\beta$-form, provided that they cannot show a $+M$ or a $-M$ effect. Accordingly, the SR group stabilises the $\alpha\beta$-form and the SOR and SO_2R groups destabilise it in accordance with the magnitude of their $-I$ effects.

The equilibrium relations among nitro-olefins and phosphorus-containing olefins have been little investigated. According to the available data [27–30], regardless of substitution, an equilibrium mixture of nitro-olefins contains appreciable amounts of $\beta\gamma$-isomers (13–19% for the systems $CH_2{=}CHCH(CH_3)NO_2 \rightleftharpoons CH_3CH{=}C(CH_3)NO_2$ [27] or $CH_2{=}C(CH_3)CH_2NO_2 \rightleftharpoons (CH_3)_2C{=}CHSO_2$). [29,30] This indicates a lower stabilisation of the $\alpha\beta$-form by the nitro-group compared with OR, SR, NR_2, COOR, CN, etc., possibly owing to the greater $-I$ effect.

Diallylphosphine is converted on refluxing with C_2H_5ONa into dipropenylphosphine in 90% yield [31]; similarly, when potassium hydroxide in methanol is employed, diallylphosphine oxide and allyl phenylphosphinic acid isomerise to dipropenylphosphine oxide and phenylpropenylphosphinic acid respectively (yield 90–95%). However, allylphosphonic acid is stable under these conditions.

Diethyl allylphosphonate isomerises completely to the propenyl isomer in the presence of sodium ethoxide even at room temperature, whereas under these conditions diethyl 3-phenylprop-2-enylphosphonate does not change and diethyl but-2-enylphosphonate gives an equilibrium mixture containing only 25% of the $\alpha\beta$-isomer [32]. Thus the phenyl and even the methyl group interacts with the double bond more strongly than the $P(O)(OC_2H_5)_2$ group. It is quite possible that in phosphine oxides and phosphinic acids the prototropic shift is due solely to the inductive effect of the PO and P(O)OH groups. Nor can one exclude in phosphines of the type R_3P the possible stabilisation of the propenyl form by the overlapping of the p orbitals of carbon with the d orbitals of phosphorus.

The capacity of various functional groups for stabilising the $\alpha\beta$-form may be estimated by comparing the equilibrium positions in systems with two different functional groups. Thus in the presence of $(C_2H_5)_3N$ an equilibrium

mixture of 34% of 1-cyano-1-ethoxy-3,3-dichloroprop-2-ene and 58% of *trans*- and 8% of *cis*-1-cyano-1-ethoxy-3,3-dichloroprop-1-ene is formed [33-35]. The equilibrium mixture of ethyl 4,4-dichlorobutenoate contains different amounts of the $\alpha\beta$- and $\beta\gamma$-isomers [35].

Under the influence of potassium ethoxide in t-butyl alcohol at 35°C, methyl *trans*-3-methoxycrotonate is almost completely converted into methyl *cis*-4-methoxybut-3-enoate [36]:

$$CH_3OCH_2CH{=}CHCOOCH_3 \rightarrow CH_3OCH{=}CHCH_2COOC_2H_5.$$

The isomer where the double bond is conjugated to the SR group predominates slightly in an equilibrium system incorporating the SCH_3 and $COOC_2H_5$ groups [36]:

$$\underset{42\%\ (trans)}{CH_3SCH_2CH{=}CHCOOC_2H_5} \rightleftarrows \underset{24\%\ (cis)\ +\ 34\%\ (trans)}{CH_3SCH{=}CHCH_2COOC_2H_5}.$$

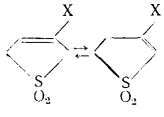
Thus the alkoxy and sulphide groups stabilise the conjugated isomer to a greater extent than the alkoxycarbonyl group. It is interesting to note that, when diethylamine acts upon the *trans*-isomer of ethyl 3,4-di(ethylthio)but-2-enoate, the latter is converted quantitatively into ethyl 3,4-di(ethylthio)but-3-enoate (a mixture of 80% of the *trans*-isomer and 20% of the *cis*-isomer), i.e. the double bond is fully displaced from conjugation with the $COOC_2H_5$ group [37].

On heating with potassium t-butoxide in dimethyl sulphoxide, an equilibrium mixture of 1% of *cis*- and 2% of *trans*-4-methoxy-1-methylthioprop-1-ene and of 32% of *cis*- and 65% of *trans*-4-methoxy-1-methylthioprop-2-ene is formed [36]:

$$CH_3OCH_2CH{=}CHSCH_3 \rightleftarrows CH_3OCH{=}CHCH_2SCH_3.$$

Thus in this case too the isomer with the double bond conjugated with the OR group is more stable, which is consistent with the relative $+M$ effects of the OR and SR groups.

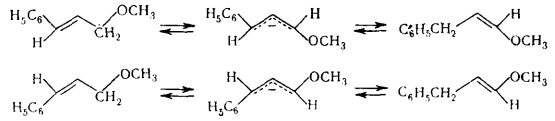
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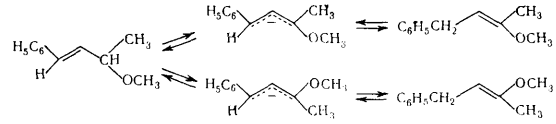
the content of the $\alpha\beta$-isomer increases in the sequence of substituents X = H ~ Cl < CH_3 ≪ OCH_3, n-C_4H_9S and in the last two cases the $\alpha\beta$-isomer predominates entirely. This can be accounted for by a donor–acceptor interaction between the substituent X, which has a free electron pair, and the sulphur atom in the SO_2 group [38].

Prototropic isomerisation is very greatly complicated by *cis–trans* isomerisation and this is why there is contradictory information in the literature about the stereochemistry of the prototropic shift. At the present time, however, it is known that prototropic isomerisation can be either stereospecific or lead to mixtures of *cis*- and *trans*-isomers depending on the structure of the olefin. It has been established that allyl ethers, for example, undergo a rigorously stereospecific isomerisation on heating with potassium t-butoxide to *cis*-propenyl ethers [5,39]. Under the reaction conditions, n-propyl *trans*-propenyl ether is not converted into the *cis*-isomer, i.e. the *cis*-isomer is indeed the primary isomerisation product.

It has recently been established [40] that the presence of substituents in the β-position has an appreciable influence on the stereochemistry of the isomerisation of allyl ethers to vinyl ethers. Thus, when potassium t-butoxide in dimethoxyethane acts at 25°C on the methyl ether of *trans*-cinnamyl alcohol, the latter gives predominantly the *cis*-isomer of 1-methoxy-3-phenylprop-1-ene (the content of the *trans*-isomer does not exceed 10%), while the methyl ether of *cis*-cinnamyl alcohol gives largely the *trans*-isomer (the content of the *cis*-isomer is about 25%):

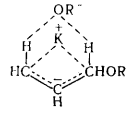


In the case of the methyl ether of 1-methylcinnamyl alcohol the isomerisation in the presence of potassium t-butoxide in dimethyl sulphoxide takes place non-stereospecifically, a mixture of different amounts of stereoisomeric vinyl ethers being formed [40]:

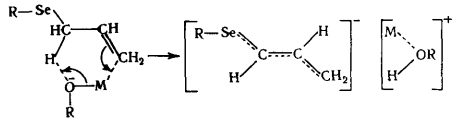


Allyl aryl selenides also isomerise stereospecifically, but in this case the *trans*-isomers are formed [10].

On the other hand, the isomerisation of allyl sulphides always leads to mixtures of 60–80% of the *cis*-isomer and 20–40% of the *trans*-isomer [8]. The differences in the stereochemistry of the isomerisation of allyl ethers, allyl sulphides, and allyl selenides are probably due to the differences in the geometry of the transition state. The formation of a stable *cis*-allyl carbanion incorporating the cation (K) [39]



has been postulated for allyl ethers. It is believed that, by virtue of the lower electronegativity and greater radius of the selenium atom, in allyl selenides the formation of a *cis*-transition complex is sterically hindered and the carbanion assumes a transoid configuration, where delocalisation of the carbanionic charge is facilitated by conjugation with the electrons in the *d* orbitals of selenium [10]:



The non-stereospecificity of the isomerisation of allyl sulphides can be explained by the fact that in this case there is a possibility of both a *cis*- and a *trans*-transition state, since sulphur is intermediate in its characteristics between oxygen and selenium.

It has been shown that, under the action of a solution of sodium in liquid ammonia, *N*-allyl-*N*-methylaniline, *N*-allyl-*N*-ethyl-*p*-toluidine, *NN*-diallylamine, etc. isomerise stereospecifically to *cis*-propenylamines. However, the compounds obtained rapidly isomerise to the thermodynamically stable *trans*-isomers even on storage in nitrogen; admixtures of alcohols or acids accelerate this process [12] and therefore in the majority of cases the isomerisation of allylamines leads to mixtures of *cis*- and *trans*-isomers (see also Riviere and Lattes [41]).

The isomerisation of $CH_2{=}CHCH(R)X$ in acetonitrile in the presence of $(C_2H_5)_2NH$ leads entirely to the formation of $CH_3CH{=}C(R)X$; there is no *cis–trans* isomerisation.

The data on the stereochemistry of this isomerisation are presented in Table 4. [15]

The stereochemistry of the reaction is independent of both the solvent (hexamethylphosphoramide, dimethyl sulphoxide, dimethylformamide, acetone, tetrahydrofuran, ether, dioxan, and others) and of the catalyst (piperidine, diethylamine, n-butylamine, isopropylamine, triethylamine, etc.) and is determined solely by the stereochemistry of the intermediate carbanion:

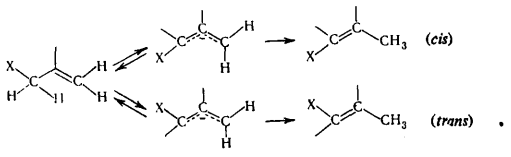
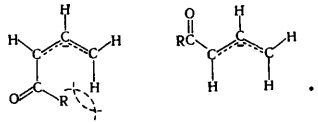


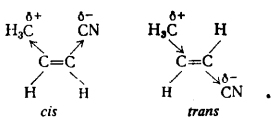
Table 4. Stereochemistry of the prototropic isomerisation $CH_2=CYCH(R)X \rightleftharpoons CH_3CY=C(R)X$.

R	X	Y	*trans*-Form, %	R	X	Y	*trans*-Form, %
H	CN	H	35	Cl	COOH	H	100
H	$COOC_2H_5$	H	85	SC_2H_5	$COOC_2H_5$	H	90
H	COOH	H	94	H	CN	Cl	6
H	COC_2H_5	H	100	H	$COOC_2H_5$	Cl	0
Cl	CN	H	90	H	COOH	Cl	0
Cl	$COOC_2H_5$	H	100				

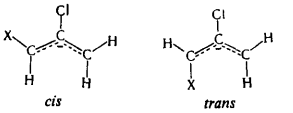
The relative amounts of the *cis*- and *trans*-isomers in the final product are determined by the ratio of the *cis*- and *trans*-carbanions, i.e. the free energies of the carbanions, the thermodynamically more stable carbanion being formed more rapidly. Evidently the thermodynamic stability of the carbanion is not necessarily the same as that of the final product. The stability of the carbanion depends on the electronic interaction between the substituents in the $\alpha\beta$- and $\alpha\gamma$-positions and on steric factors. In systems of the type $CH_2=CHCH_2X \rightleftharpoons CH_3CH=CHCHX$ the stability of the carbanion is controlled by the interaction of the $\alpha\gamma$-substituents (i.e. the H and X groups); when $X = COOC_2H_5$, COR, or COO^-, a greater stability of the *trans*-carbanion is to be expected:



By virtue of the smaller bulk of the CN group, in nitriles the interaction of the α-CN group and the γ-H atom plays a less important role; moreover, in this case the *cis*-form is stabilised by dipole–dipole interaction to a greater extent than the *trans*-form and therefore there is a possibility of the formation of a mixture of *cis*- and *trans*-isomers in proportions corresponding to the stabilities of the intermediate carbanions:



For a system of the type $CH_2=OClCH_2X \rightleftharpoons CH_3CCl=CHX$, the interaction of the substituents in the $\alpha\beta$-positions promotes the formation of the *cis*-carbanion:



These considerations proved to be valid also in the study of other systems, for example $CH_2=C(SR)CHClCOOC_2H_5 \rightleftharpoons CH_3(SR)=CClCOOC_2H_5$ or $CH_3=C(SR)CH(SR')COOC_2H_5 \rightleftharpoons CH_3C(SR)=C(SR')COOC_2H_5$. [42]

The carbanionic mechanism of prototropic isomerisation has been confirmed by a number of experimental findings. Thus the isomerisation of allyl or propenyl derivatives in deuteroalcohols always leads to the formation of α- or γ-deutero-derivatives respectively [17,43-45]. For example, the following reaction takes place on refluxing in deuterobutanol in the presence of potassium t-butoxide [43]:

$$CH_2=CHCH_2OR \rightarrow \underset{27.8\%}{CH_3CH=CHCH_2OR} + \underset{69.7\%}{CH_2DCH=CHCH_2OR} + \underset{2.5\%}{CHD_2CH=CHCH_2OR}$$
$$(R = C_9H_{19})$$

Similarly at room temperature we have the reaction [44]

$$C_9H_{19}CH_2CH=CHS(O)CH_3 \rightarrow C_9H_{19}CH=CHCD_2S(O)CH_3 .$$

At 175 °C deuterium exchange takes place and an equilibrium is established [43]:

$$CH_2=CHCH_2OR \rightleftarrows \underset{47\%}{CH_3CH=CHOR} + \underset{40\%}{CH_2DCH=CHCHOR} + \underset{11\%}{CHD_2CH=CHOR} + \underset{1.3\%}{CD_3CH=CHOR}.$$

All these data are consistent with a carbanionic mechanism:

$$CH_2=CHCH_2X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_2^-CH=CHX \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CH_3CH=CHX$$
$$k_1 > k_2,\ k_{-1} > k_{-2}$$

Kinetic studies on prototropic isomerisation [15,46,47] also confirm the carbanionic mechanism. The rate of isomerisation depends on the affinity of the catalyst for the proton [47]. For the system

$$CH_2=C(R)CH(R')X \rightleftarrows CH_3C(R)=C(R')X$$ [15]

the reaction obeys second-order kinetics. Certain data on the effect of the nature of the base on the rate of isomerisation in this system are presented in Table 5, which shows that the catalytic activity of amines depends on the degree of substitution at the nitrogen atom (the rate of isomerisation increases with decreasing steric hindrance at the nitrogen atom) and on solvation [the more solvated primary amines are less active than the less solvated $(C_2H_5)_2NH$].

The basicity of the catalyst is also of great importance. Thus 1,3-diphenylprop-2-en-1-ol isomerises only under the action of alcoholic alkali but not pyridine or triethylamine [48], while the isomerisation of 1,3,3-triphenylprop-2-en-1-ol requires the use of potassium t-butoxide in dimethyl sulphoxide but not aqueous alkali [49].

The rate of reaction depends very markedly on the nature of the solvent, reaching a maximum in aprotic polar solvents (hexamethylphosphoramide, dimethylformamide, dimethyl sulphoxide, acetonitrile, etc.)[15], which is typical of reactions with a carbanionic mechanism. Table 6 presents certain data on the effect of solvents on the rate of isomerisation.

The rate of reaction is determined by the formation of the carbanion. All factors facilitating the formation of the carbanion increase the rate of reaction. Thus in the $CH_2=CHCH_2X$ system the rate of isomerisation increases in the following sequence of X: $COOH < COOC_2H_5 < CN < COR$, which is the same as the familiar series of substituents with increasing $-M$ effects [15] and can be accounted

for by the facilitation of the heterolysis of the α-C–H bond. The introduction of a chlorine atom into the α-position of the system increases the rate of isomerisation owing to the *–I* effect and the acceleration of the reaction in the presence of chlorine in the β-position is due to the additional stabilisation of the carbanion by the involvement of lone-pair electrons of the chlorine atom in delocalisation[15]. The systems examined above are characterised by low activation energies (about 10 kcal) and highly negative activation entropies (about –35 e.u.), which indicates a high degree of order in the transition state. It has been suggested[15] that in the transition state the formation of the B–H bond preceeds the heterolysis of the highly polarised α-C–H bond and the transition state itself is a highly solvated still incompletely dissociated ion pair.

Table 5. Rate of isomerisation and the nature of the base $CH_2=CRCHR'COOC_2H_5 \rightarrow CH_3CR=CR'COOC_2H_5$*.

Base	R=H, R'=Cl** k, litre mole^{-1} s^{-1}	R=Cl, R'=H*** k, litre mole^{-1} s^{-1}
$(C_2H_5)_2NH$	0.90	0.092
n-$C_4H_9NH_2$	0.51	0.039
iso-$C_3H_7NH_2$	0.35	0.032
iso-$(C_3H_7)_2NH$	0.12	0.0116
$(C_2H_5)_3N$	0.09	0.0123

*The reaction carried out in ether at 24.7°C, goes to completion.
**Only the *trans*-isomer is formed.
***Only the *cis*-isomer is formed.

Prototropic isomerisation in the presence of bases has found wide application in organic synthesis. Several novel methods are based on the isomerisation of unsaturated alcohols where the alcoholic group is converted into a carbonyl group as a result of prototropic shift:

$$RCH=CHCH(OH)R' \rightarrow RCH_2CH=C(OH)R' \rightarrow RCH_2CH_2COR' .$$

The conversion of allyl alcohols themselves into carbonyl compound has found only limited application in the synthesis of aliphatic-aromatic ketones stable to alkalis (for example, see Refs. 46–48). However, a prototropic shift in substituted allyl alcohols constitutes the foundation of several preparative syntheses.

Thus when hot dilute alkalis act upon the cyanohydrin of ββ-diphenylacrolein or the amide of 2-hydroxy-4,4-diphenylbut-3-enoic acid, prototropic isomerisation is accompanied by the hydrolysis of the nitrile and amide groups and the formation of α-oxo-γγ-diphenylbutyric acid in high yields[50]:

$$(C_6H_5)_2C=CHCH(R)OH \rightarrow (C_6H_5)_2CHCH=C(R)OH \rightarrow (C_6H_5)_2CHCH_2COCOOH ,$$

where R = CN or $CONH_2$. This method is of general importance for the synthesis of α-ketoacids.

A prototropic shift is the rate-determining stage in the synthesis of succinic acid by refluxing β-formylacrylic acid with a solution of potassium cyanide, which takes place according to the following mechanism[51]:

$$HOOCCH=CHCHO \xrightarrow{CN^-} HOOCCH=CHCH(CN)OH \rightarrow HOOCCH_2CH=C(CN)OH \rightarrow$$
$$\rightarrow HOOCCH_2CH_2COCN \xrightarrow{OH^-} HOOCCH_2CH_2COOH .$$

A similar mechanism constitutes the basis of a simple method for the synthesis of esters of β-substituted propionic acids by the action of an excess of acetone cyanohydrin and triethylamine on αβ-unsaturated aldehydes with electron-accepting substituents in the β-position[52]. The intermediate cyanohydrin isomerises to a β-ketonitrile, which in the presence of an excess of acetone cyanohydrin or alcohol (as a solvent) gives an ester of propionic acid:

$$RCH=CHCHO \xrightarrow{CN^-} RCH=CHCH(CN)OH \rightarrow RCH_2CH=C(CN)OH \rightarrow$$
$$\rightarrow RCH_2CH_2COCN \xrightarrow{R'O^-} RCH_2CH_2COOR' .$$

Table 6. Effect of solvents on the rate of isomerisation. $CH_2=CHCHClCOOC_2H_5 \rightarrow CH_3CH=CClCOOC_2H_5$*.

Solvent	k, litre mole^{-1} s^{-1}	Solvent	k, litre mole^{-1} s^{-1}
Hexamethylphosphoramide	instantaneous reaction	Tetrahydrofuran	0.35
Dimethylformamide	reaction ends after 5 min	Monoglyme	0.084
Acetonitrile	2.47	Ether	0.0136
Acetone	1.99		

*The base is $(C_2H_5)_2NH$; temperature 0.2° ± 0.2°C.

The intermediate formation of the cyanohydrin is confirmed by the fact that, when acetone cyanohydrin and triethylamine act on the cyanohydrin of cinnamaldehyde, an ester of β-phenylpropionic acid is also formed[53].

In the reaction of cinnamaldehyde and α-methylcinnamaldehyde with deuteroacetone cyanohydrin in the presence of triethylamine, 75–80% of the deuterium enters into the α-position of the ester. Thus the transfer of hydrogen in this case takes place largely intramolecularly:

$$C_6H_5CH=CHCH(CN)OH \xrightleftharpoons{:B} C_6H_5\overset{B}{\overset{\vdots}{C}}H\cdots CH=C(CN)O^- \rightarrow$$
$$C_6H_5CH_2CH=C(CN)O^- \xrightarrow{BD} C_6H_5CH_2CHDCOCN \xrightarrow{RO^-} C_6H_5CH_2CHDCOOR .$$

When polyene aldehydes take part in the reaction, the process involves only the αβ-double bond[54]; in this way, it is possible to synthesise αβ-dihydro-derivatives:

$$R(CH=CH)_nCHO \rightarrow R(CH=CH)_{n-1}CH_2CH_2COOR' ,$$

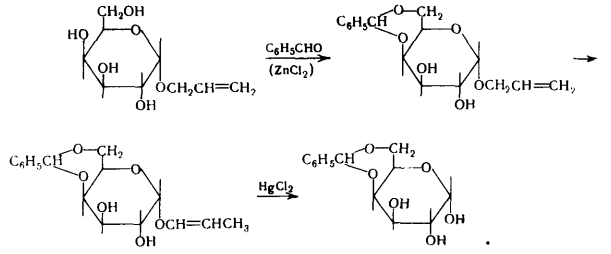
where R = CH_3, C_6H_5, or $COOC_2H_5$, and n = 2 or 3.

The isomerisation of allyl ethers has found fairly wide application in the synthesis of propenyl ethers (for examples, see Refs. 5–7 and 55–59). Among the catalysts proposed, potassium t-butoxide is particularly effective when dimethyl sulphoxide is used as a solvent[5,6,58]. The isomerisation of allyl ethers by heating with potassium t-butoxide is a convenient preparative method for the synthesis of propenyl ethers especially those which are difficult to obtain by other methods—ethers derived from polyhydric alcohols. For example, tetrapropenylpentaerythritol was obtained from tetra-allylpentaerythritol in about 83% yield[5]:

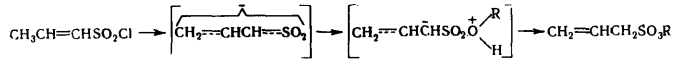
$$C(CH_2OCH_2CH=CH_2)_4 \rightarrow C(CH_2OCH=CHCH_3)_4 .$$

The easy isomerisation of allyl ethers to propenyl ethers suggested the use of the allyl group as a protecting group in carbohydrate chemistry[60–65]. After the necessary operations, the allyl ether isomerises to the propenyl ether and its protecting group is removed in a suitable way

(by acid hydrolysis, ozonolysis, oxidation by alkaline potassium permanganate, and by treatment with $HgCl_2$). The allyl protecting group is particularly convenient in the synthesis of benzyl and benzylidene derivatives of sugars. Thus 4,6-*O*-benzylidene-D-galactose can be obtained from 1-allyl-D-galactopyranoside [65]:



An interesting method for the synthesis of esters of $\beta\gamma$-unsaturated sulphonic acids otherwise difficult to obtain is based on the alcoholysis of $\alpha\beta$-unsaturated sulphonyl chlorides in the presence of triethylamine [66]. The reaction involves a mechanism with prototropic isomerisation via sulphenes.



In the presence of triethylamine, allyl aryl sulphones isomerise smoothly to propenyl sulphones [67,68]. Thus on heating allyl β-naphthyl sulphone in dioxan or alcohol with triethylamine for 15–17 h, β-naphthyl propenyl sulphone was obtained:

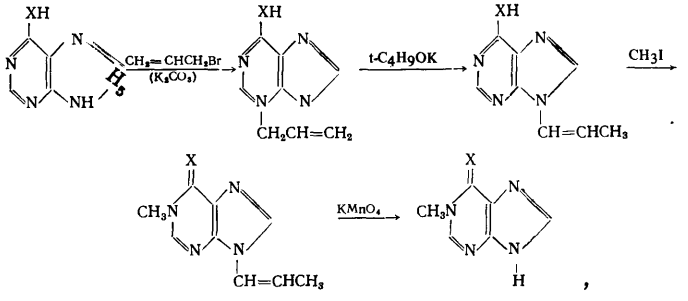
$$\beta\text{-}C_{10}H_7SO_2CH_2CH{=}CH_2 \rightarrow \beta\text{-}C_{10}H_7SO_2CH{=}CHCH_3 \ .$$

The isomerisation of allylamines in the presence of potassium t-butoxide in dimethyl sulphoxide [11,12], a dispersion of sodamide on alumina in pentane or hexane [69], or a solution of sodium in liquid ammonia [70] at room temperature is a very convenient method for the synthesis of *NN*-disubstituted enamines in high yields (60–100%):

$$CH_2{=}CHCH_2NRR' \rightarrow CH_3CH{=}CHNRR' \ .$$

A method has been developed for the synthesis of *N*-propenylpyrrolidinone and *N*-propenylcaprolactam in 50–80% yield by the isomerisation of the corresponding allyl derivatives at 165–180°C in the presence of potassium t-butoxide [71]. *N*-Allylthiolactams isomerise in the presence of potassium t-butoxide in dimethyl sulphoxide even at room temperature [72].

The use of the allyl group to protect the amino-group in purine bases has been suggested [73]. 1-Methyladenine and 1-methylhypoxanthine have been obtained using such protection via the 9-allyl derivatives by the mechanism



where X = O or NH.

A prototropic shift constitutes the basis of a new method for the synthesis of iminoethers by the action of potassium cyanide and primary amines on $\alpha\beta$-unsaturated aldehydes in the presence of potassium hydroxide or sodium methoxide in methanol at room temperature [74]. The reaction takes place by the mechanism

$$RCH{=}CHCHO \rightarrow RCH{=}CHCH(CN)NHR' \rightarrow RCH_2CH{=}C(CN)NHR' \rightarrow \rightarrow RCH_2CH_2C(OCH_3){=}NR' \ .$$

$\alpha\beta$-Unsaturated aldehydes react by a similar mechanism with acetone cyanohydrin and primary or secondary amines with formation of α-cyanoimines or α-cyanoenamines respectively [75]:

$$RCH{=}CHCHO \rightarrow RCH{=}CHCH(CN)NR' \rightarrow RCH_2CH{=}C(CN)NHR' \rightarrow RCH_2CH_2C(CN){=}NR'$$
$$RCH{=}CHCHO \rightarrow RCH{=}CHCH(CN)NR'R'' \rightarrow RCH_2CH{=}C(CN)NR'R'' \ .$$

The intermediate formation of aminonitriles has been demonstrated by their synthesis in the reaction of cinnamaldehyde with acetone cyanohydrin and piperidine, morpholine, or aniline [75,76]:

$$C_6H_5CH{=}CHCHO \rightarrow C_6H_5CH{=}CHCH(CN)R \ ,$$

where R = NCH_6H_5 diagrams.

When potassium cyanide in methanol was allowed to react with cinnamaldehyde cyanohydrin, methyl β-phenylpropionate was obtained [77].

1-Cyano-1-piperidino-3-phenylprop-1-ene isomerises smoothly to an enaminonitrile on being passed through an alumina column [76]; a product with the hydrogen atom and the amino-group in *cis*-positions is formed.

The product of a prototropic shift was obtained on refluxing 3-chloro-3-*p*-nitrophenylprop-1-ene in benzene with triethylamine [78]:

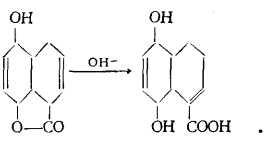
$$p\text{-}O_2NC_6H_4CHClCH{=}CH_2 \rightarrow p\text{-}O_2NC_6H_4CCl{=}CHCH_3 \ .$$

The formation of small amounts of an ester of but-1-enylmethylphosphinic acid on methylation of but-2-enylphosphonic ester can also be accounted for by a prototropic shift [79]:

$$CH_3CH{=}CHCH_2P(O)(OC_3H_7\text{-iso})_2 \xrightarrow{CH_3I} CH_3CH{=}CHCH_2P(CH_3)(O)(OC_3H_7\text{-iso})$$
$$CH_3CH_2CH{=}CHP(CH_3)(O)(OC_3H_7\text{-iso})$$

The formation of methyldiphenyl-(1-phenylprop-1-enyl)-phosphonium iodide on methylation of diphenyl-(1-phenylallyl)phosphine can be interpreted similarly [80].

Isomerisation in the presence of bases is used for the synthesis of $\alpha\beta$-unsaturated acids, esters, nitriles, lactones, ketones, etc. from the corresponding $\beta\gamma$-derivatives (for examples, see Refs. 81–86). For instance, *cis*-5,8-dihydroxy-1,4,5,8,9,10-hexahydronaphthoic acid is obtained by refluxing with aqueous alcoholic alkali the 1,8-lactone of *cis*-5,8-dihydroxy-3,4,5,8,9,10-hexahydronaphthoic acid [86]:



When nucleophilic agents act upon $CHCl{=}CHCH_2X$, [87] $CH_2{=}CClCH_2X$, [80,81] or $CH_2{=}CHCHClX$, [87] other reactions, apart from prototropic isomerisation, can occur depending on the reactant, the position of the chlorine atom, and the reaction conditions. Thus, regardless of the configuration of the initial compound, hydrolysis of $CHCl{=}CHCH_2COOC_2H_5$ by aqueous alkali leads to the formation

of *trans*-3-chlorocrotonic acid, i.e. the isomerisation and hydrolysis take place with retention of the chlorine atom:

$$CHCl{=}CHCH_2COC_2H_5 \rightarrow CH_2ClCH{=}CHCOOH \ .$$

When the reaction is carried out in alcoholic solution, isomerisation with simultaneous addition of the alcohol and retention of the chlorine atom takes place:

$$CHCl{=}CHCH_2COOC_2H_5 \rightarrow CH_3ClCH(OC_2H_5)CH_2COOC_2H_5 \ .$$

However, on refluxing with an aqueous solution of sodium carbonate, the shift of the double bond is accompanied by the exchange of the chlorine atom for a hydroxy-group:

$$CHCl{=}CHCH_2X \rightarrow CH_2(OH)CH{=}CHX \ ,$$

where X = CN or $COOC_2H_5$.

In the case of $CH_2 = CClCH_2X$ the isomerisation takes place with retention of the chlorine atom or its replacement, depending on the nature of X; moreover, in a number of instances an elimination reaction is observed[87,88]:

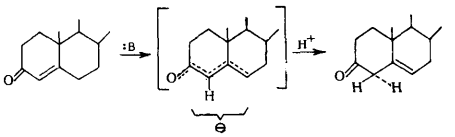
$$CH_2{=}CClCH_2COOC_2H_5 + C_2H_5O^- \rightarrow CH_3C(OC_2H_5){=}CHCOOC_2H_5 \ ,$$
$$CH_2{=}CClCH_2N + C_2H_5O^- \rightarrow CH_3CCl{=}CHCN + CH_3C(OC_2H_5){=}CHCN \ .$$

Isomerisation with or without replacement of the chlorine atom and sometimes the formation of addition products occur with $CH_2{=}CHCHClX$:[87]

$$CH_2{=}CHCHClCOOC_2H_5 + (C_2H_5)_2NH_2 \rightarrow CH_3CH{=}CClCOOC_2H_5 \ ,$$
$$CH_2{=}CHCHClCOOC_2H_5 + C_2H_5ONa \rightarrow CH_3CH{=}CClCOOH + CH_3CH{=}CClCOOC_2H_5 + $$
$$+ CH_3CH(OC_2H_5)CHClCOOC_2H_5 \ .$$

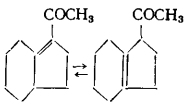
Base-catalysed isomerisation is used to convert Δ^5-3-oxosteroids into Δ^4-3-oxosteroids. Thus Δ^5-pregnenedione has been converted in high yield into progesterone[89].

A method has also been developed for the conversion of Δ^4-3-oxosteroids into Δ^5-3-oxosteroids. For this purpose, Δ^4-3-oxosteroids are heated with potassium t-butoxide in t-butyl alcohol and the resulting carbanions are then protonated by acetic acid, forming Δ^5-3-oxosteroids[90]:

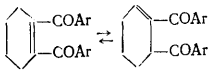


The reaction is based on the fact that in this case protonation at the C_4 atom is faster than at the C_6 atom. This possibility is confirmed by the fact that, on refluxing, for example, 6,6-dimethylcyclohex-2-enone with deuterium oxide, the vinyl hydrogen atom is exchanged 170 times faster than the allyl hydrogen atom[91]. This method has been used to prepare 17α-methyl-Δ^5-androst-17β-en-2-one from 17-methyltestosterone. Ketones with several conjugated bonds remain unchanged when treated in this way[90].

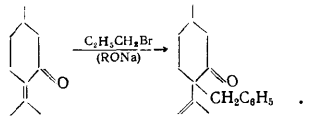
It is interesting that on heating (for 24 h) 1-acetyl-$\Delta^{1,8}$-perhydroindane with potassium methoxide in methanol, an equilibrium mixture is formed containing 80% of the $\Delta^{8,9}$-isomer[92]:



Similarly, on heating (72 h) with a potassium hydroxide solution, 1,2-diaroylcyclohexene is converted to the extent of 90% into 1,6-diaroylcyclohexene[93]:

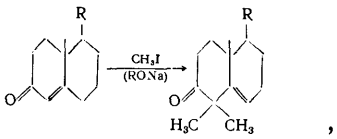


The different reactivities of the α- and β-positions of carbanions with functional groups are used in the synthesis of α-alkyl and $\alpha\alpha$-dialkyl-substituted $\beta\gamma$-unsaturated acids, esters, ketones, etc. by alkylating the $\alpha\beta$-unsaturated isomers in an alkaline medium (for examples, see Refs. 94–109). Thus the alkylation of sorbic acid in liquid ammonia with CH_3I in the presence of potassamide leads to 2,2-dimethylhexa-3,5-dienoic acid[94]. The alkylation of ketones with a tetrasubstituted ethylene bond by alkyl halides in the presence of sodium alkoxides gives α-monoalkyl derivatives[96,97]. For example:



α-Monoalkyl derivatives can also be obtained by maintaining specially selected reaction conditions[98,99]. Thus, a 44% yield of 4-methyltestosterone is obtained by the gradual addition of 1.2 equivalents of methyl iodide to testosterone in boiling t-butyl alcohol in the presence of 1.5 equivalents of potassium t-butoxide.

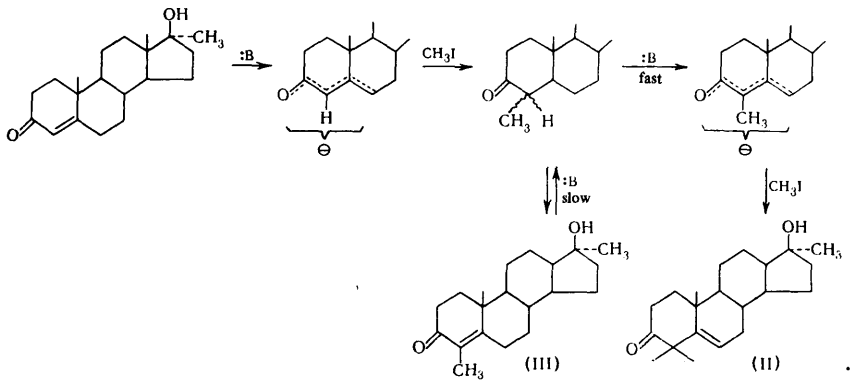
Dialkylation of $\alpha\beta$-unsaturated cyclic ketones has found extensive application in the chemistry of terpenes and steroids. Thus bicyclic ketones, which are necessary for the synthesis of terpenes of the labdanolic acid type[100] or triterpenes of the β-amyrin type[101], were obtained via the mechanism



where R = H or OH.

Alkylation of cholestenone with CH_3I in t-butyl alcohol in the presence of potassium t-butoxide leads to 4,4-dimethylcholest-5-en-3-one[102,105]; 4,4-dimethylandrost-3-ene[106] and 4,4-dimethylergosta-5,7,22-trien-3-one[107] were obtained in this way from testosterone and ergosterone respectively; 3-oxo-Δ^4-derivatives of androstene and pregnane are methylated similarly[108].

The formation of dialkyl derivatives is explained by the fact that secondary alkylation and (or) the formation of a tertiary carbanion are faster than the primary alkylation and (or) the formation of a secondary carbanion. In fact, the reaction of CH_3I with the carbanion formed from the ketone (I) by brief treatment with potassium t-butoxide leads to the ketone (II) in 74% yield, while methylation of the α-methyl ketone (III) under the same conditions gives the ketone (II) in a yield of only 6%:[110]



When alcohols are allowed to react with the chlorides of $\alpha\beta$-unsaturated acids in the presence of tertiary amines, the main reaction products are esters of vinylacetic acid[111,112]:

$$RCH_2CH{=}CHCOCl + R'OH\,(R'_3N) \rightarrow RCH{=}CHCH_2COOR' + RCH_2CH{=}CHCOOR' .$$

The nature of the amine and the structure of the acid chloride (Table 7) affect the ratio of the $\alpha\beta$- and $\beta\gamma$-isomers.

Table 7. Effect of the nature of the amine and the structure of the acid chloride on the ratio of the $\alpha\beta$- and $\beta\gamma$-isomers $CH_2{=}C(R)CH_3COOCH_2$(IV)$\rightleftharpoons CH_3C(R){=}CHCOOCH_3$(V).

Amine	pK	Mixture composition, %			
		IV, R=H	V, R=H	IV, R=CH_3	V, R=CH_3
Triethylamine	10.7	87.8	12.2	83.1	16.9
N-Ethylpiperidine	10.4	83.5	16.4	89.6	10.4
Triallylamine	8.3	47.5	52.5	44.1	55.9
N-Ethylmorpholine	7.7	65.3	34.7	69.1	30.9
Pyridine	5.2	1.6	98.4	0.6	99.4

The results show that the ratio of the reaction products is controlled by the initial abstraction of a proton. It has been suggested that, when highly basic amines ($pK > 10$) are employed, the reaction takes place via the following mechanism[112]:

$$RCH_2CH{=}CHCOCl + R'_3N \rightarrow RCH_2CH{=}CHCON^+R'_3Cl^- \rightarrow$$

$$\left[RCH{-}CH{=}CH{-}C{=}O\right] \rightarrow [RCH{=}CHCH{=}C{=}O] \xrightarrow{R'OH} RCH{=}CHCH_2COOR .$$

Thus the reaction consists in the prototropic isomerisation of the intermediate acylammonium salt with elimination of an NR_3 group and the formation of a keten, which then combines with the alcohol.

It has been shown in recent years[113-116] that prototropic isomerisation is also the basis of the Varrentrapp reaction, which is carried out by heating *cis*- or *trans*-unsaturated acids with central double bonds at 300–360°C with potassium hydroxide in an inert atmosphere; this results in the formation of acetic and a saturated acid containing two carbon atoms less than the initial unsaturated acid:

$$CH_3(CH_2)_n CH{=}CH(CH_2)_m COOH \rightarrow CH_3(CH_2)_{n+m} COOH + CH_3COOH + H_2 .$$

Thus palmitic acid was obtained from oleic or petroselinic acid in yields of 80–85% and 78% respectively, nonanoic acid was obtained from undec-10-enoic acid in 80% yield, and heptanoic acid was obtained from non-2-enoic acid in 80% yield also.

A detailed study of the Varrentrapp reaction using oleic acid as an example showed that the prototropic shift plays the main role and that in the initial stages the migration of double bonds takes place to an equal extent on either side. However, when, as a result of a series of reversible shifts, the double bond reaches the $\alpha\beta$-position, a reversible cleavage takes place and the entire system of equilibria is displaced towards the carboxy-group. The overall reaction mechanism may be represented thus:

$$R(CH_2)_{n-1}CH{=}CH(CH_2)_{n+1}COO^- \rightleftharpoons R(CH_2)_{n-1}CH{\cdots}\bar{C}H{\cdots}CH(CH_2)_mCOO^- \rightleftharpoons$$

$$R(CH_2)_nCH{=}CH(CH_2)_mCOO^- \rightleftharpoons R(CH_2)_nCH{\cdots}\bar{C}H{\cdots}CH(CH_2)_{m-1}COO^- \rightleftharpoons$$

$$R(CH_2)_{n+1}CH{=}CH(CH_2)_{m-1}COO^- \rightleftharpoons \cdots\cdots \rightleftharpoons$$

$$R(CH_2)_{n+m-1}CH{\cdots}\bar{C}H{\cdots}CHCOO^- \rightleftharpoons R(CH_2)_{n+m}CH{=}CHCOO^- \rightarrow$$

$$R(CH_2)_{n+m}COOH + CH_3COOH + H_2 .$$

III. ISOMERISATION IN THE PRESENCE OF ACIDS

It has been known for a long time that the prototropic shift of the double bond in olefins can be induced by acids. The reaction involves the intermediate formation of a carbonium cation and is frequently accompanied by allyl isomerisation and structural changes. For this reason, acid-catalysed isomerisation has found much less application than base-catalysed isomerisation. The overall process mechanism can be represented as follows:

$$H^+ + \underset{|}{\overset{|}{C{=}C{-}C{-}H}} \rightleftharpoons H{-}\underset{|}{\overset{|}{C}}{-}\overset{+}{\underset{|}{\overset{|}{C}}}{-}\underset{|}{\overset{|}{C}}{-}H \rightleftharpoons H{-}\underset{|}{\overset{|}{C}}{-}\underset{|}{\overset{|}{C{=}C}} + H^+ .$$

The acid-catalysed isomerisation of allyl alcohols to carbonyl compounds[117], which has found industrial application for the synthesis of isobutyraldehyde from 2-methylprop-2-en-1-ol[118], has been most thoroughly investigated. It has been shown that, as in base-catalysed isomerisation, the reaction depends appreciably on the structure of the allyl alcohol. The allyl alcohol itself and its linear homologues of the type $RCH{=}CHCH_2OH$ are hardly isomerised on refluxing with 0.44 *N* sulphuric acid solution[110,111]. On the other hand, β-alkylallyl alcohols are smoothly converted in high yields (88–92%) into aldehydes:

$$CH_2{=}CH(R)CH_2OH \rightarrow CH_3CH(R)CHO ,$$

where R = CH_3, C_2H_5, iso-C_3H_7, or t-C_4H_9.

$\beta\gamma$-Substituted allyl alcohols undergo simultaneously a prototropic shift (the formation of aldehydes) and oxotropic isomerisation (formation of ketones), the latter predominating judging from the yields:

$$RCH{=}C(R')CH_2OH \rightarrow RCH_2CH(R')CHO + RCOCH(CH_3)R'$$

R	R′	Yield of aldehyde, %	Yield of ketone, %	R	R′	Yield of aldehyde, %	Yield of ketone, %
CH_3	CH_3	25	63	CH_3	C_2H_5	36	52
C_2H_5	CH_3	15	71	n-C_3H_7	C_2H_5	19	69

Alcohols of the type $RR'C{=}CR''CH_2OH$ are readily dehydrated. Secondary alcohols of the type $CH_2{=}C(R)CH(R')OH$ are smoothly converted into ketones:

$$CH_2{=}C(R)CH(R')OH \rightarrow CH_3CH(R)COR' \text{ (yield 86–92\%)}$$

Only traces of aldehydes—products of oxotropic rearrangement with a subsequent prototropic shift—are observed.

The prototropic isomerisation of secondary alcohols of the type $RCH{=}C(R')CH(R'')OH$ also takes place without complications:

$$RCH{=}C(R')CH(R'')OH \rightarrow RCH_2CH(R')COR''$$

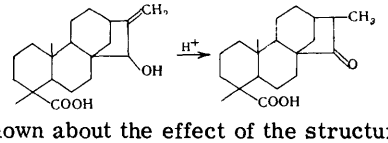
The study of the kinetics and the effect of the acidity of the medium on the rate of conversion of β-alkylallyl alcohols into aldehydes and of the kinetics of the conversion of the glycols $CH_3C(R)(OH)CH_2OH$ into the same aldehydes confirms the carbonium ion mechanism of the acid isomerisation of allyl alcohols [119–121]:

$$CH_2{=}C(R)CH_2OH + H_3O^+ \longrightarrow CH_3\overset{+}{C}(R)CH_2OH \longrightarrow CH_3\overset{+}{C}(H)\text{–}C(OH)H(R) \longrightarrow$$

$$CH_3C(R){=}CHOH \longrightarrow CH_3CH(R)CHO$$

Thus the proton adds to the double bond with subsequent elimination of a proton from the α-position. This mechanism is consistent with the results of the isomerisation of 1-[^{14}C]methylallyl alcohol, which leads to the formation of isobutyraldehyde labelled with carbon-14 at the carbonyl group [122].

The acid-catalysed isomerisation of alcohols has found limited application in the synthesis of certain cycloalkanones [123] and certain complex cyclic ketones [124,125]. For example:

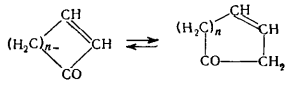


Little is known about the effect of the structure of the olefin on the equilibrium position in acid-catalysed isomerisation in $RCH_2CH{=}CHX \rightleftharpoons RCH{=}CHCH_2X$ systems. It has been noted that the $\alpha\beta$-isomer predominates in the equilibrium mixture of aliphatic ketones [126]:

$$(CH_3)_2C{=}CHCOCH{=}C(CH_3)_2 \rightleftarrows (CH_3)_2C{=}CHCOCH_2C(CH_3){=}CH_2 \rightleftarrows$$
$$\sim 93\% \qquad\qquad \sim 7\%$$
$$\rightleftarrows CH_2{=}C(CH_3)CH_2COCH_2C(CH_3){=}CH_2$$
$$\text{traces}$$

However, in the hydrolysis of *cis*-β-chlorocrotononitrile with sulphuric acid at room temperature, the amide of *cis*-β-chlorovinylacetic acid was obtained in high yield [83].

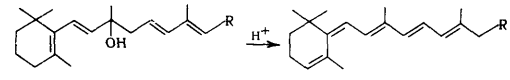
The equilibrium between cycloalk-2-enones and cycloalk-3-enones on refluxing in benzene in the presence of p-$CH_3C_6H_4SO_3H$ depends on ring size [127]:



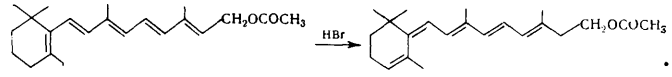
n	Time of attainment of equilibrium, h	Composition of equilibrium mixture, %	
		$\alpha\beta$-isomer	$\beta\gamma$-isomer
3	fast.	99.0	1.0
4	1	73.0	27.0
5	2	20.0	80.0
6	22	0.3	99.7

The shift of equilibrium towards the $\beta\gamma$-isomer with increasing number of units is probably associated with the fact that the double bond and the carbonyl group become non-coplanar. This leads to the destabilisation of the $\alpha\beta$-isomer, which in the absence of conjugation is thermodynamically less stable than the $\beta\gamma$-isomer. An approximate estimation of the angle of rotation Θ between the planes of the CO group and the double bond on the hypothesis that the difference between the chemical shifts in the H NMR spectrum of cyclonones $\gamma_B - \gamma_A$ (A = H at C_2 and B = H at C_3) is proportional to $\cos\Theta$, showed that Θ increases progressively with the number of units in the ring [127]. Possibly this is due to the fact that, on increasing the number of units, the conformations where the CO group and the double bond are located in the same plane become hindered, as shown, for example, by the conformational analysis of cyclo-oct-2-enone, in which full coplanarity of the CO group and the double bond is achieved only in the model where there should be strong *trans*-annular interaction between the H atom at C_4 and the *cis*-H atom at C_8.

In connection with the problem of the synthesis of biologically active preparations of the type of vitamin A, a detailed study was made of the acid-catalysed prototropic isomerisation in the vitamin A series, which has been called retroionylidene rearrangement. This rearrangement takes place in the acid-catalysed dehydration of hydroxy-derivatives and when acidic reagents act upon compounds where the side chain is fully conjugated with the ring double bond and consists in the shift of the entire conjugated bond system from the functional group towards the ring [128–131]:

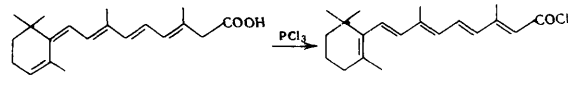


where R = CH_2OCH_3, CHO, COOR, etc.;



This results in the formation of biologically inactive species—the so called retroionylidene structures. The rearrangement is due to the fact that in a molecule of the vitamin A type there is appreciable steric interaction between the methyl groups of the ring and the side chain; when acted upon by acids, such compounds should be converted into the thermodynamically more stable retroionylidene compounds. The transition from such structures to ionylidene compounds is possible on treatment with alkaline agents (potassium hydroxide, sodium hydroxide, alkoxides, etc.) or by chromatography on aluminosilicate columns [130,132,133].

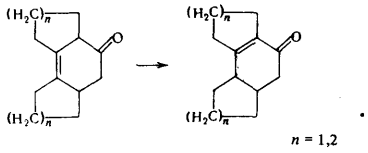
Acids with the retroionylidene structure are converted into straight-chain acid chlorides on treatment with specially purified phosphorus trichloride [132]. For example:



Acid-catalysed prototropic isomerisation may complicate many processes. Thus the hydration of divinylacetylenes in aqueous solutions in the presence of sulphuric acid and mercuric sulphate results in the formation of divinyl ketones instead of the expected allyl vinyl ketones [134]:

$$RCH{=}CHC{\equiv}CCH{=}CHR' \rightarrow RCH{=}CHCOCH{=}CHCH_2R' \ .$$

A method has been proposed for the synthesis of $\alpha\beta$-unsaturated tricyclic ketones by refluxing the $\beta\gamma$-isomers with a 3% methanol solution of hydrogen chloride or a 0.1% benzene solution of p-$CH_3C_6H_4SO_3H$. [135] 4-Oxo-$\Delta^{8a(8)}$-decahydro-*as*-indacene and 9-oxo-$\Delta^{4(8a)}$-dodecahydrophenanthrene were obtained in this way:



$n = 1,2$

A method has also been proposed for the synthesis of aryl propenyl sulphones by heating allyl aryl sulphones with a solution of boron trifluoride in sulphuric acid [136]:

$$ArSO_2CH_2CH{=}CH_2 \rightarrow ArSO_2CH{=}CHCH_3 \ (43\text{—}50\%) \ .$$

IV. ISOMERISATION IN THE PRESENCE OF METAL CARBONYLS

It has been established by investigations in recent years that metal carbonyls [$Fe(CO)_5$,[137-141] $CoH(CO)_4$,[142] or $Co(CO)_8$ [143]] are effective catalysts of the prototropic isomerisation of substituted olefins with functional groups; they may contain functional groups with free electron pairs (allyl alcohols [137-140,142] and allyl ethers [140,141]) or they are esters of unsaturated acids capable of π–π conjugation [141]. The principal advantage of metal carbonyls is the fact that in their presence the reaction may be carried out in a neutral medium (although examples are also known where the reaction was carried out in the presence of alkalis). [137] Thus this method may be used to achieve the shift of double bonds when the initial or final products are sensitive to acids and alkalis.

The isomerisation of unsaturated alcohols has been most thoroughly investigated. Secondary allyl alcohols isomerise particularly smoothly on heating with 10–20 mole % $Fe(CO)_5$ without a solvent at 110–125°C or on refluxing in octane. The yields of ketones reach 60–80%: [140]

$$CH_2{=}C\,(R)\,CH\,(OH)\,R' \rightarrow CH_3CH(R)COR' \ .$$

Alcohols of the type $CH_2{=}CH(CH_2)nCH(OH)R$ enter into the reaction with equal success [140].

However, primary alcohols and cyclohex-2-enol gives low yields of products under these conditions. The yield increases to 29–54% when the reaction is carried out in pentane at room temperature in the presence of 3–5 mole% $Fe(CO)_5$ with simultaneous ultraviolet irradiation [140]. For example:

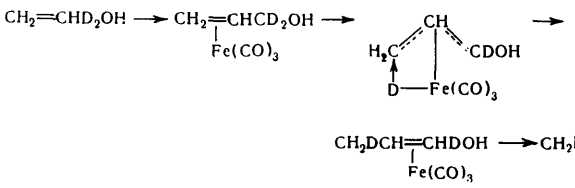
$$RCH{=}CH\,(CH_2)_n\,CH_2OH \rightarrow R\,(CH_2)_{n+2}\,CHO \ ,$$

where $n = 1$ and R = C_2H_5 (*cis*-isomer) (29%) or $n = 7$ and R = H (54%).

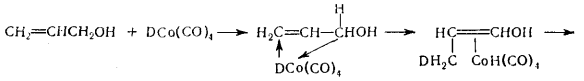
The isomerisation of allyl, crotyl, and other unsaturated alcohols in the presence of $CoH(CO)_4$ is complicated by hydroformylation and leads to low yields (3–21%) of carbonyl compounds [142].

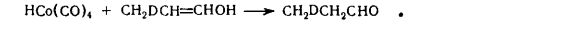
On heating (to 130–160°C) with $Fe(CO)_5$, cyclo-oct-3-enol and cinnamyl alcohol give cyclo-octanone and 3-phenylpropionaldehyde in yields of 90 and 100% respectively.

As regards the reaction mechanism, it is suggested that initially the allyl system and the metal carbonyl form a π-complex [138,142,144,145], within which a 1,3-hydrogen transfer takes place. This is confirmed by the fact that, in the isomerisation of 1,1-dideuteroallyl alcohol in the presence of $Fe(CO)_5$, only 1,3-dideuteropropionaldehyde is formed [144]:



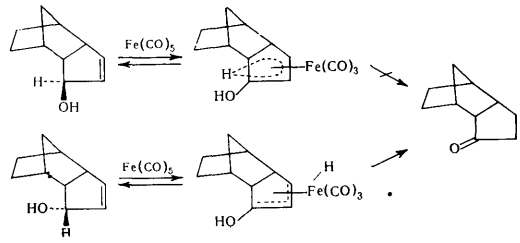
This mechanism is also confirmed by the formation of 3-deuteropropionaldehyde in the isomerisation of allyl alcohol in the presence of $CoD(CO)_4$: [142]





Possibly the π-complex exists in equilibrium with a δ-complex.

Additional confirmation of the mechanism of the rearrangement via the formation of a π-complex between the allyl system and the metal carbonyl was obtained in a study of the isomerisation of *endo*-α-1-hydroxy-5,6-dihydrocyclopentadiene to *endo*-β-1-hydroxy-5,6-dihydrocyclopentadiene. It was found that the first compound does not isomerise on heating with iron pentacarbonyl even at 160°C, while the second gives the ketone in about 40% yield on heating to 130°C for 16 h with 10% of iron pentacarbonyl in an atmosphere of nitrogen [145]:



This shows that the rearrangement takes place via a π-complex, since in both cases the attack by the iron carbonyl can take place from the least screened *exo*-side, but only in the second case is there a possibility of the formation of a transition state in which a hydrogen atom can be readily transferred.

The isomerisation of allyl ethers takes place quantitatively in the presence of 5 mole % $Fe(CO)_5$ in pentane under ultraviolet illumination [140,146]. This leads to the formation of a mixture of approximately equal amounts of the *cis*-isomer (44–52%) and the *trans*-isomer (48–56%). Under these conditions, diallyl ether gives a mixture of 26%, 42%, and 31% of *cis*, *cis*-; *cis*, *trans*-; and *trans*, *trans*-dipropenyl ethers respectively [146] and 1-methoxybut-3-ene forms a mixture of products of complete and partial isomerisation:

$$CH_2{=}CHCH_2CH_2OCH_3 \rightarrow \underset{25\%}{CH_3CH{=}CHCH_2OCH_3} + \underset{34\%\ cis+41\%\ trans}{CH_3CH_2CH{=}CHOCH_3} \ .$$

The stability of the tautomers was estimated by studying their relative amounts in isomerisation mixtures of different types derived from unsaturated ethers (Table 8).[140] The Table shows that the $\alpha\beta$-isomers of ethers in which the double bond is conjugated to the ether group are the most stable. The ratio of the Δ^3-isomer and the Δ^2-isomer is 1.5 : 1 both for open-chain and cyclic ethers, which indicates an important role of the inductive destabilisation of the $>CHOCH_3$ group.

Table 8. Relative amounts of tautomers in isomerisation mixtures of ethers.

Initial ether	Total yield, %	Relative amounts of isomers, %			
		Δ^1	Δ^2	Δ^3	Δ^4
$CH_3OCH{=}CH(CH_2)_2CH_3$	91	84.0	6.0	9.0	1
$CH_3O(CH_2)_3CH{=}CH_2$	90	85.0	5.0	9.0	1
	93	93.5	3.9	3.6	
	96	95.0	2.0	3.0	

In the isomerisation of ethers of the type $CH_2{=}CH(CH_2)_nOCH_3$ (n = 1, 2, 3, 4, 8, 9) there is an increase of the overall amount of isomers with more remote double bonds and a decrease of the content of the $\alpha\beta$-isomer in the equilibrium mixture. The ratio of the vinyl ether to each non-conjugated isomer (with the exception of the $\beta\gamma$-isomer) is approximately 10 : 1. Calculation shows that the replacement of the alkyl group by a methoxy-group at the vinyl carbon atom increases the stability of the isomer by 1.5 kcal.

Table 9. Relative amounts of tautomers in isomerisation mixtures of esters.

Ester	Relative amounts of esters in mixture, %						
	Δ^1	Δ^2	Δ^3	Δ^4	Δ^5	Δ^6	Δ^7
$C_5H_{11}CH{=}CHCOOCH_3$	...	18.1	8.1	20.4	23.6	28.5	1.5
$C_2H{=}CH(CH_2)_5COOCH_3$	...	17.8	7.3	20.8	24.2	28.7	1.2
	88.8	3.6	7.6	—	—	—	—
	86.8	4.4	8.8	—	—	—	—

Table 9 presents certain data on the relative amounts of tautomers obtained in the isomerisation of esters by refluxing in octane in the presence of 10–20 mole % $Fe(CO)_5$.[141] The equilibrium ratio of the $\alpha\beta$- and $\beta\gamma$-isomers of the octenoates is 2.5 : 1 according to the data obtained. However, the overall sum of the Δ^4-, Δ^5-, and Δ^6-isomers exceeds the content of the $\alpha\beta$-isomer, because the $-M$ and $-I$ effects of the $COOCH_3$ group do not affect the stability of the internal isomers stabilised mainly by hyperconjugation.

Among cyclic isomers, the $\alpha\beta$-isomer stabilised by the $-M$ affect of the $COOCH_3$ group and hyperconjugation is the most stable. It has recently been established that $Fe(CO)_5$ is an effective catalyst of the isomerisation of N-allylimides to N-propenylimides[147].

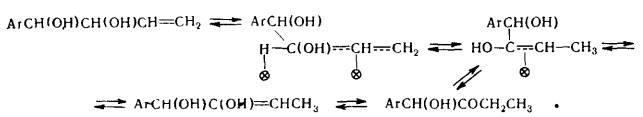
V. ISOMERISATION IN THE PRESENCE OF VARIOUS CATALYSTS

The catalytic isomerisation of olefins with functional groups can be of preparative or industrial value, but, although it was described long ago[117], it has not been adequately investigated. The literature quotes almost exclusively examples of isomerisation under conditions of heterogeneous catalysis. Thus it has been noted that allyl and crotyl alcohols are converted into propionaldehyde and butyraldehyde respectively when the alcohol vapours are passed over copper or cobalt at 150–400°C.[148–150] Vinyl glycols of the type $ArCH(OH)CH(OH)CR{=}CHR'$ (Ar = C_6H_5 or α-furyl) passed in the vapour phase at 200°/15 mmHg over Cu/Cr_2O_3[151,152] or 5–10% $Pd/CaCO_3$[153] give the ketols $ArCH(OH)COCHRCH_2R'$ in yields of 30 to 65% in addition to other products. Similarly, when the vapour of the glycol $CH_3CH{=}CHCHOHCHOHCH{=}CHCH_3$ is passed over Cu/Cr_2O_3 at 130°/15 mmHg, dibutyryl is formed in 45% yield[154].

A promising method has been proposed for the catalytic isomerisation of N-alkylallylamines to N-alkylpropenylamines in 26–50% yield when the vapour is passed at 260 to 270°C over alumina promoted by potassium hydroxide; at the same time 5–15% of N-alkylidenealkylamines is formed[155]:

$$CH_2{=}CHCH_2NHR \rightarrow CH_3CH{=}CHNHR + CH_3CH_2CH{=}NR \ .$$

Vinyl glycols of the type $ArCH(OH)CH(OH)CH{=}CH_2$ are also isomerised on simple distillation over $Pd/CaCO_3$[156] or reduced copper[152], forming the ketols $ArCH(OH)COC_2H_5$ (yield 62–75%). The following possible mechanism of the formation of ketols under the conditions of heterogeneous catalysis, the first stage of which is adsorption of the unsaturated molecule on the catalyst metal, has been proposed:



The isomerisation of allyl alcohols and glycols takes place also on distillation over Raney nickel. Thus n-valeraldehyde was obtained in 80% yield from pent-3-enol[157] and methyl 12-oxostearate was obtained from methyl ricinoleate[158]. It is suggested that in this case the alcohol may be dehydrogenated with subsequent hydrogenation of the double bond.

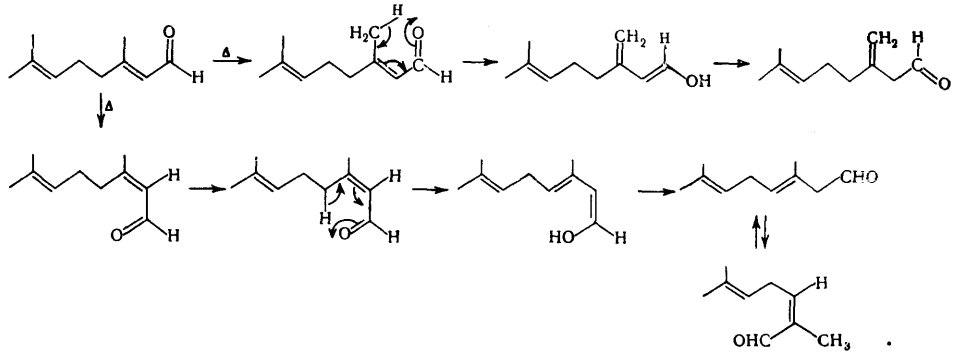
The conversion of allyl alcohols into aldehydes was observed in the reduction by zinc treated with alkali[159] or by the Zn/Cu couple[160]. In some cases there is a possibility of isomerisation under conditions of homogeneous catalysis. Thus phenylvinylglycol is converted into 1-hydroxy-1-phenylbutan-2-one on heating in solution with cis-$PdCl_2[P(C_6H_5)_3]_2$:[151]

$$C_6H_5CH(OH)CH(OH)CH{=}CH_2 \rightarrow C_6H_5CH(OH)COC_2H_5 \ .$$

The yield greatly depends on the nature of the solvent, reaching 85–100% in dimethylformamide. In benzene, diglyme, and nitromethane the reaction scarcely occurs, in chloroform the yield of the ketol is 10–12%, and in ethylene glycol and hexamethylphosphoramide the yield is 20–30%. Saturated glycols do not change under the experimental conditions. Probably the isomerisation takes place via the formation of a π-complex.

VI. THERMAL ISOMERISATION

The thermal prototropic isomerisation has been little investigated. For example, citral (a mixture of *cis*- and *trans*-isomers in proportions of 2 : 1) isomerises on heating (130–175°C) in a vacuum (15–130 mmHg) to isocitral (also a mixture of the *cis*- and *trans*-isomers) in yields up to 70% and 3-methylene-7-methyloct-6-enal in yields up to 30%. An intramolecular cyclic electron transfer mechanism has been proposed for the thermal isomerisation of citral, isocitral being formed from the *cis*-form of citral and 3-methylene-7-methyloct-6-enal from the *trans*-form of citral [162]:



The thermal isomerisation of nitro-olefins at 110–140°C, which leads to the formation of equilibrium mixtures [163] (Table 10), was investigated in greater detail. The data in Table 10 show that in the case of unsubstituted nitro-olefins or derivatives substituted only in the α-position the equilibrium is wholly displaced towards the $\alpha\beta$-isomer. The effect of substituents in the β- or γ-positions results in the appearance in the equilibrium mixture of appreciable amounts of the $\beta\gamma$-isomer. The equilibrium position is also influenced by the nature of the solvent: polar aprotic solvents promote a shift of equilibrium towards the $\beta\gamma$-isomer (Table 11).

Table 10. Thermal isomerisation of nitro-olefins $RCH_2C(R')=C(R'')NO_2 \rightleftharpoons RCH=C(R')CH(R'')NO_2$.

R	R′	R″	Content in equilibrium mixture, %	
			$\alpha\beta$-isomer	$\beta\gamma$-isomer
H	H	H	100	0
CH_3	H	H	86	14
H	CH_3	H	75	25
H	H	CH_3	100	0
H	CH_3	CH_3	90	10

The study of the thermal isomerisation of vinylnitriles [164] showed that unsubstituted nitriles or derivatives with substituents in the α- or β-positions only do not isomerise. In the presence of two methyl groups or electron-accepting substituents (C_6H_5, C_6H_5O) in the γ-positions the equilibrium is displaced towards the $\beta\gamma$-isomer:

$$RR'CHC(R'')=C(R''')CN \rightleftarrows RR'C=C(R'')CH(R''')CN .$$

R	R′	R″	R‴	$\alpha\beta$-isomer %	$\beta\gamma$-isomer %
H	H	H	H	100	0
H	H	$CH_3(C_6H_5)$	H	100	0
H	H	H	$CH_3(C_6H_5)$	100	0
CH_3	CH_3	H	CH_3	100	0
CH_3	CH_3	H	H	28	72
C_6H_5	H	H	H	36	64
C_6H_5O	H	H	H	5	95

However, the γ-substituted nitrile does not isomerise when there is a methyl group in the α-position.

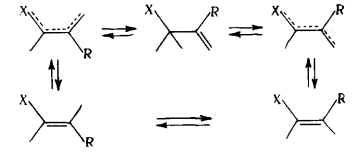
The stereochemistry of the thermal isomerisation of nitriles is independent of temperature and solvent. In the initial stages of the process the *cis*-isomer predominates and the *trans*/*cis* ratio increases only in the course of the reaction, which can be readily accounted for by the *cis*–*trans* isomerisation occurring simultaneously. As a result, the ratio of the *cis*- and *trans*-isomers established is approximately 1.4.

Table 11. Effect of solvents on the position of equilibrium in the system $(CH_3)_2C=CHNO_2 \rightleftharpoons \rightleftharpoons CH_2=C(CH_3)CH_2NO_2$.

Solvent	Temp., °C	Content in equilibrium mixture, %	
		$\alpha\beta$-isomer	$\beta\gamma$-isomer
Cyclohexane	140	83	17
Benzene	140	80	20
Toluene	140	75	25
Acetonitrile	140	75	25
Dioxan	140	67	33
Dimethyl sulphoxide	25	68	32
Hexamethyl-phosphoramide	25	52	48

The rate of reaction increases in the following series of solvents: toluene < dioxan < acetonitrile < dimethyl sulphoxide ≪ hexamethylphosphoramide [164].

The stereochemistry of the reaction and the effect of solvents on the rate of reaction and also the effect of substituents and solvents on the position of equilibrium are consistent with a carbanion mechanism of the thermal isomerisation [163,164]:

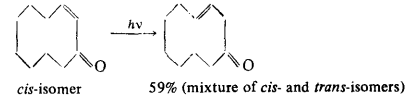


VII. PHOTOCHEMICAL ISOMERISATION

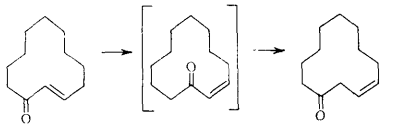
A fairly large number of examples of the migration of the double bond in carbonyl compounds under the influence of ultraviolet light have now been described. The principal feature of the photochemical isomerisation is that in this case the shift of the double bond takes place always from a conjugated to a non-conjugated position, i.e. the $\beta\gamma$-isomer is formed from the $\alpha\beta$-isomer. Thus, on irradiation of 4,5,5-trimethylhex-3-en-2-one, the product is pure 4-methylene-5,5-dimethylhexan-2-one, which on standing is spontaneously partially converted into vinyl ketone, giving an equilibrium mixture in proportions of 1 : 1.[165]

The study of the photochemical isomerisation of aliphatic $\alpha\beta$-unsaturated ketones of the type RR'C=C(R'')COCH$_3$ in ether showed[166] that ketones without substituents or containing substituents in the α- or β-positions only or simultaneously in the γ- and α- or β-positions do not isomerise. On the other hand, γ-substituted ketones readily enter into the reaction. Thus 5-methylhex-4-en-2-one was obtained in 75% yield from 5-methylhex-3-en-2-one, while hex-3-en-2-one gave a mixture of the *cis*- and *trans*-isomers of hex-4-enone[166]. When phorone is irradiated in methanol or hexane, 2,6-dimethylhepta-1,5-diene-4-one is formed in high yield[167,168] together with traces of 2,6-dimethylhepta-1,6-diene-4-one.

The results of the photolysis of $\alpha\beta$-unsaturated cyclic ketones are related to ring size[169]. In the case of cyclodec-2-enone[170] and cyclododec-2-enone[171] the double bond migrates from the $\alpha\beta$- to the $\beta\gamma$-position:



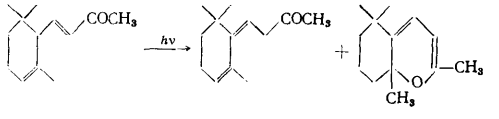
cis-isomer 59% (mixture of *cis*- and *trans*-isomers),



trans-isomer *cis*-isomer 92%.

Before isomerisation *trans*-isomers are converted into the *cis*-form. After prolonged irradiation of *cis*-cyclodec-2-enone, 2-vinylcyclo-octanone was formed in a yield up to 35% in addition to the cyclodec-3-enone.

Several examples of the photochemical shift of the double bond in the α-ionone series have been described[172,173]. However, the reaction is frequently complicated by the formation of bicyclic structures. For example:



Photochemical isomerisation has been used to convert 7-oxocholesteryl acetate into 3β-acetoxycholest-4-en-7-one[174] and 10α-testosterone into 17α-hydroxy-3-oxo Δ^5-10α-androstene[175].

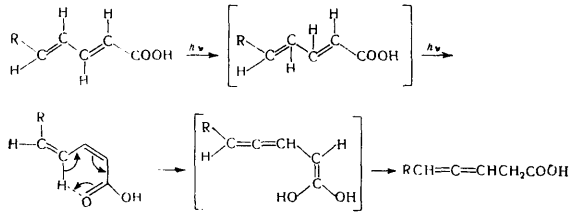
It has been noted that, when crotonaldehyde vapour is irradiated at 30°C with light at 245–400 nm, vinylacetaldehyde is formed[176].

Esters of crotonic, pent-2-enoic, 4-methylpent-2-enoic, and 2-methylcrotonic acids are smoothly isomerised on illumination with ultraviolet light, giving quantitative yields of vinylacetic ester and its substituted derivatives[177]. Under the same conditions, ethyl 1,3-dimethylcrotonate gives ethyl 2,3-dimethylbut-3-enoate with a yield of only 7%. The reaction is promoted by polar solvents, low concentrations of the reactants, and high temperatures.

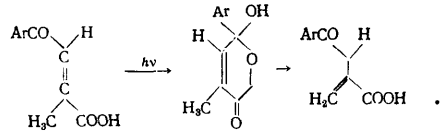
An interesting method for synthesising allenic acids of the type RCH=C=CHCH$_2$COOH is based on the photochemical reaction of dienoic acids (sorbic and penta-2,4-dienoic) in ether in the presence of traces of formic acid[178]. The yield of the final product is 20–32%:

$$RCH{=}CHCH{=}CHCOOH \rightarrow RCH{=}C{=}CCH_2COOH .$$

Salts of the acids do not isomerise under these conditions, which indicates an important role of the unionised carboxy-group in the reaction. The following mechanism has been proposed for the isomerisation:

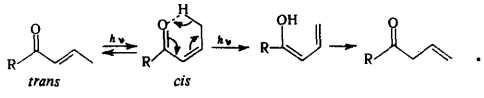


The isomerisation of α-methyl-β-aroylacrylic acids under the influence of sunlight takes place with deconjugation of the aroyl group[179]:



The process proceeds via the lactone, which can be isolated when the reaction is interrupted at the initial stage.

In accordance with all available data for the mechanism of photochemical reactions[169,180], it is believed that the photochemical isomerisation of $\alpha\beta$-unsaturated carbonyl compounds to $\beta\gamma$-isomers takes place by the mechanism (for the *trans*-isomers)



This mechanism has been confirmed by the fact that the isomerisation of $(CH_3)_2CHCH{=}CHCOCH_3$ in deuteromethanol (CH_3OD) resulted in 90% conversion into deuterated $\beta\gamma$-unsaturated ketone, where 90% of the hydrogen in the 3-position was replaced by deuterium, which is possible only when the process proceeds via the enol [$(CH_3)_2C{=}CHCH_2COCH_3$ does not exchange hydrogen in the 3-position for deuterium under identical conditions].[166]

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Zelinskii Institute of Organic Chemistry,
Moscow