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Reactivity of terpenes and their analogues in an 'organised medium'

N F Salakhutdinov, V A Barkhash

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Abstract. Published studies on the reactivity of terpenes and their analogues in an 'organised medium', viz. upon adsorption on solid catalysts and upon complex formation with cyclodextrins (photochemical processes), are analysed. It is shown that the use of an 'organised medium' not only improves the environmental characteristics of the known processes involving natural terpene derivatives. In addition, due to the specific features of the latter (conformational mobility, polyfunctionality), it opens broad opportunities for discovering unusual transformations, and this extends the prospects of using the 'renewable raw materials' for fine organic synthesis. The bibliography includes 92 references.

I. Introduction

'Fixing' of substrates through their adsorption on solid catalysts or due to complex formation with cyclodextrins are among the methods for influencing the reactivity of chemical compounds in thermal or photochemical processes that have been vigorously developing in recent years. This approach makes it possible to change sharply the selectivity of a process by creating steric hindrance in certain parts of the molecule or by imparting conformational rigidity to the molecule. In addition, adsorption of organic substrates on solid catalysts often changes the activation barriers to many transformations; in the case of molecules with multivariant reactivity, this makes it possible to direct the reaction along a previously unknown route.

Whereas reactions of aromatic compounds in the 'fixed state' have been intensely studied for a fairly long period,[1,2] studies on the reactivity of terpenoids under these conditions are still at their early stage. However, it can be said with confidence that the number of works devoted to this topic will sharply increase, firstly, because researchers will attempt to extend the range of substrates that can be involved in these reactions and, secondly, because terpenoids are promising compounds, which can undergo new unusual transformations due to their polyfunctionality and conformational flexibility.

This review appears to be the first attempt to summarise the accumulated experimental results in this interesting field of organic chemistry.

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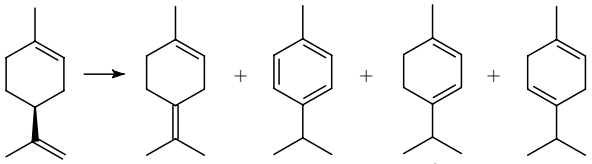
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II. Intramolecular reactions

1. Isomerisation of terpenoids on solid catalysts

Acid-catalysed rearrangements of terpenoids in various homogeneous media (from weakly acid to superacid) have been studied fairly comprehensively (see, for example, Ref. 3). In this Section, we consider the rearrangements of terpenoids on solid catalysts, which have been used with increasing frequency in recent years, in place of Lewis and Brønsted acids, for isomerisation of organic compounds.

Tanaka *et al.*[4] have studied the transformations of limonene **1** in the presence of various metal oxides and phosphates at 60 °C under normal pressure.



1 **2** **3** **4** **5**

Basic (MgO), acid-base (ZrO_2, Al_2O_3, and TiO_2-ZrO_2) and weakly acidic ($AlPO_4$, Nb_2O_5) catalysts proved to be inactive in this reaction. The other catalysts used in this study (including 96% H_2SO_4) led to the formation of mixtures of products containing terpinolene **2** (the main product) and **3**–**5** in various ratios.[4] The $SiO_2-Al_2O_3$ and SO_4^{2-}/ZrO_2 systems proved to be the most active catalysts; the use of the latter results in fairly selective (up to 84%) formation of the compound **2**. The researchers believe that both Lewis and Brønsted acid sites are active in this reaction; however, better selectivity with respect to terpinolene is achieved in the case of catalysts having strong Lewis sites. At the same time, the strong solid Lewis acid SO_4^{2-}/Fe_2O_3 does not exhibit catalytic activity in this reaction, and this prompts the thought that the dependence of the degree of conversion of the compound **1** on the characteristics of the catalyst used is more complex.

A number of patents [5–10] have been devoted to isomerisation of α-pinene **6**, β-pinene **7** and turpentine containing these terpenes in the presence of X-type zeolites. This process leads to a mixture of products, which contains limonene **1** as the major component.

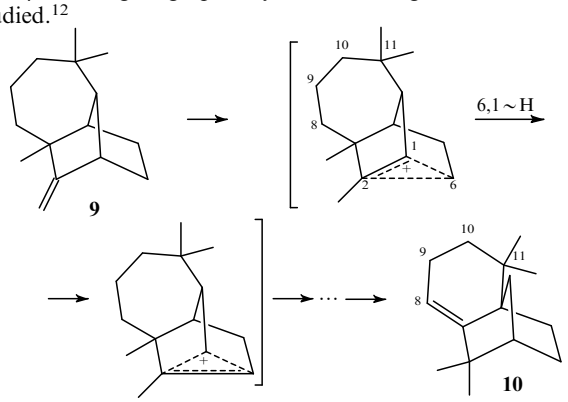


6 **7** **8**

When this transformation is carried out at 150 – 175 °C, the yield of limonene amounts to 50% – 65%; the reaction mixture also contains camphene **8** (15% – 20%) and terpinolene **2**

(~10%). It has been found[11] that the use of KX zeolite leads to better results than the use of the NaX, CaX and NH_4X zeolites.

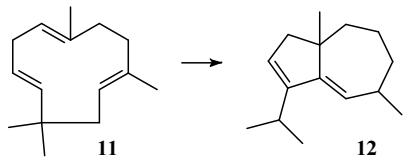
The isomerisation of optically active longifolene **9** on the wide-pore β-zeolite giving optically active isolongifolene **10** has been studied.[12]



9 **10**

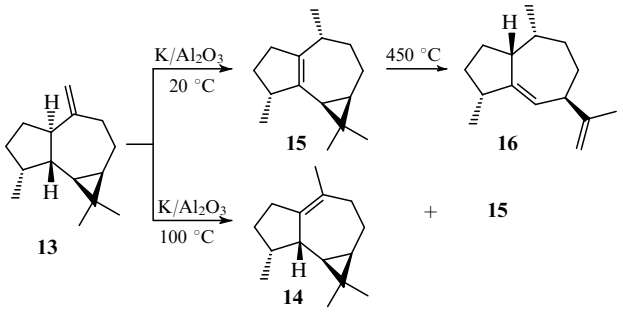
Polovinka *et al.*[13] who have compared isomerisation on zeolites with transformations of the compound **9** in a superacid medium, have found that in the latter case, the degenerate rearrangement with 1,2-shift of the C(8)–C(11) bridge occurs more rapidly than the non-degenerate 6,1-hydride shift, and this gives the racemic compound **10**. Evidently, in the case where zeolite is used, the opposite relationship between the rates of these processes is observed, which results in the retention of the optical activity.

α-Humulene **11** also isomerises in the presence of β-zeolite: at 20 °C it is converted into bicyclohumulene **12** in 60% yield over a period of 1.5 h.[14]



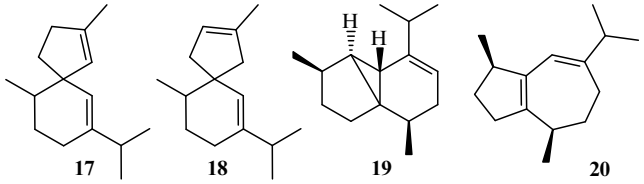
11 **12**

When (+)-aromadendrene **13** is kept at room temperature over alumina with deposited potassium, it is converted quantitatively into (−)-isoledene **15**. If this reaction is carried out at 100 °C, (+)-ledene **14** is formed in addition to the compound **15**. The alkene **15** is thermally unstable and is converted into (+)-γ-gurjunene **16** on heating to 450 °C.[15]



13 **15** **16** **15** **14**

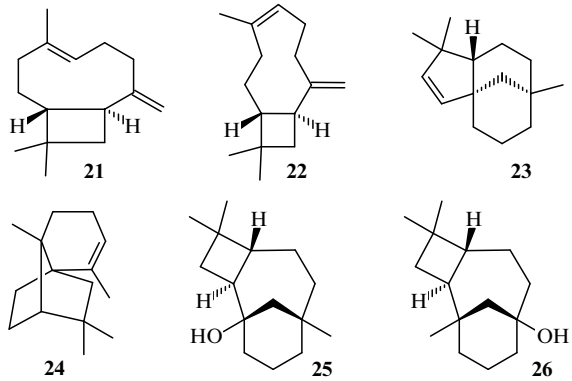
Isomerisation of the alkene **14** in the presence of the solid superacid SO_4^{2-}/TiO_2 (10 min, 20 °C) has led to 7-isopropyl-2,10-dimethylspiro[4,5]deca-1,6-diene **17** and its isomer, 7-isopropyl-2,10-dimethylspiro[4,5]deca-2,6-diene **18**.[16] It was suggested that these compounds are formed intermediately during the more extensive isomerisation of ledene **14** in formic acid.



17 **18** **19** **20**

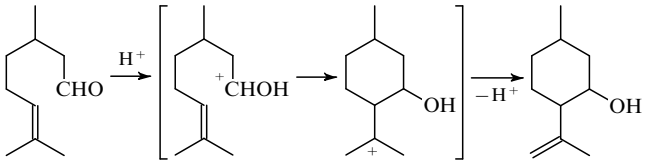
The same products were obtained in the isomerisation of (1*S*,4*R*,5*R*,6*S*,10*R*)-7-isopropyl-4,10-dimethyltricyclo[4.4.0.0^{1,5}]-dec-7-ene **19**. It was found[16] that the alkene **16** adsorbed on SO_4^{2-}/ZrO_2 isomerises at room temperature into (6*R*,10*R*)-3-isopropyl-6,10-dimethylbicyclo[5.3.0]deca-1(7),2-diene **20**.

The transformations of caryophyllene **21** and isocaryophyllene **22** on acid alumina lead mostly to clovene **23** and α-neoclovene **24**, respectively.[17] Caryophyllene **21** not only isomerises to clovene **23** but is also hydrated to give alcohols, caryolan-1-ol **25** and isocaryolan-8-ol **26**.



21 **22** **23** **24** **25** **26**

Considerable attention of researchers is paid to isomerisation of terpenoids containing functional groups, *i.e.* aldehydes, ketones, alcohols or epoxides of the terpene series. Cyclisation of citronellal **27** to isopulegol **28** in the presence of acidic zeolites such as clinoptilolite, mordenite and fojazite in various solvents at 61–84 °C has been studied.[18] A possible mechanism of this process includes the protonation of the carbonyl group, the interaction of the carbocation centre with the 6,7-double bond and abstraction of a proton yielding the alcohol **28**.

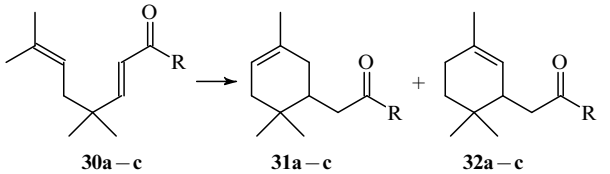


27 **28**

The reaction mixture contains also a small amount of di(2-isopropenyl-5-methylcyclohexyl) ether **29** resulting from bimolecular dehydration of the alcohol **28**.

Salakhutdinov *et al.*[19] have studied the behaviour of some dienones — analogues of terpene derivatives — on the NH_4Y- and β-zeolites in order to elucidate the dependence of the reaction route on the structure of the initial ketone and the reaction conditions.

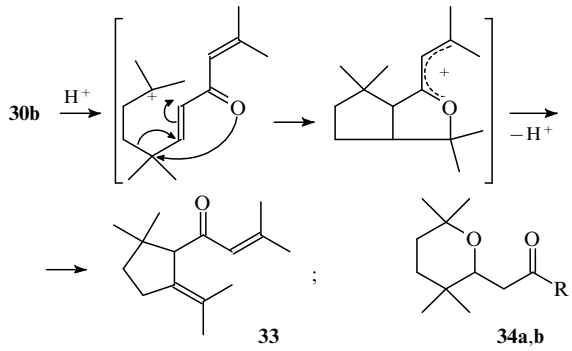
The transformation of ketones **30a–c** in the presence of NH_4Y zeolite (60–80 °C) gives rise to mixtures of compounds **31a–c** and **32a–c**, respectively.



30a–c **31a–c** **32a–c**

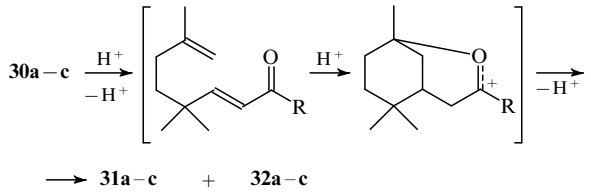
R = Me (**a**), CH = C(Me)$_2$ (**b**), Bu^i (**c**).

In the case of trienone **30b**, 3-isopropylidene-1,1-dimethyl-2-(1-oxo-3-methylbut-2-enyl)-cyclopentane **33** is formed, in addition to the compounds **31b** and **32b**. When the wide-pore β-zeolite is used as the catalyst and the substrate is adsorbed on the catalyst by a different method, the ketones **30a** and **30b** are converted into compounds **34a** and **34b**, respectively.

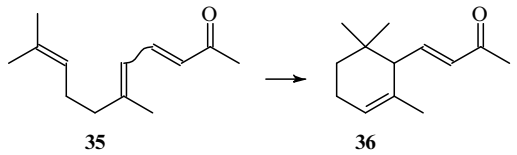


A possible mechanism of the transformations of the ketones **30a–c** is presented in Scheme 1.

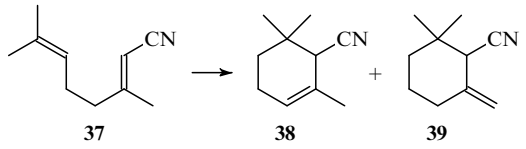
Scheme 1



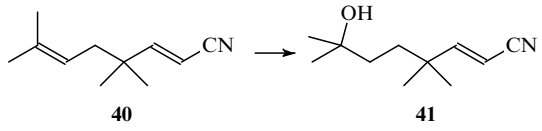
The use of the CaY zeolite made it possible to solve a problem of practical importance, namely, to carry out selective cyclisation of pseudoionone **35** to α-ionone **36**.



Cyclisation of 2,6-dimethyl-1,5-heptadienecarbonitrile has been reported.[21] When this compound is applied on the β-zeolite at room temperature, it is converted almost immediately into cyclic nitriles **38** and **39**.

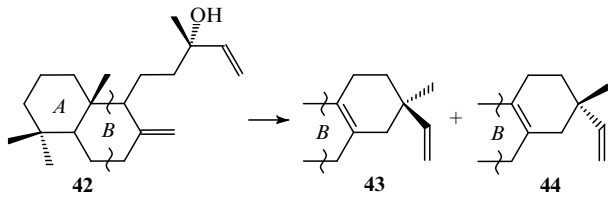


Prolonged keeping of nitrile **40** under the same conditions does not lead to any cyclic products; instead, the arising carbocation reacts with a nucleophile from the reaction medium to give alcohol **41**.

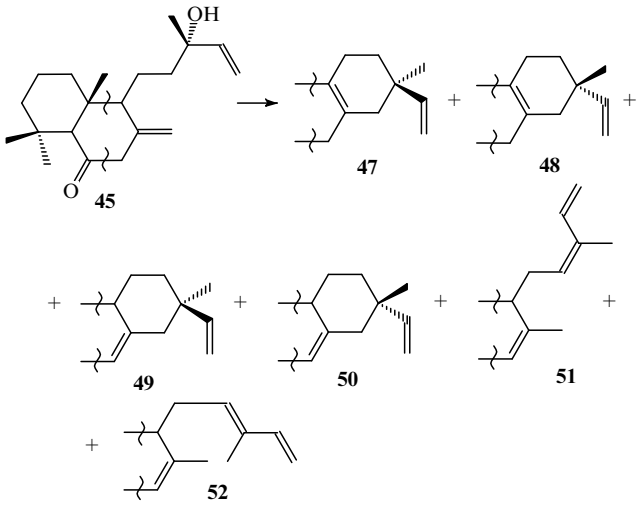


A study devoted to the transformations of labdane alcohols on the HY zeolite has been reported.[22]

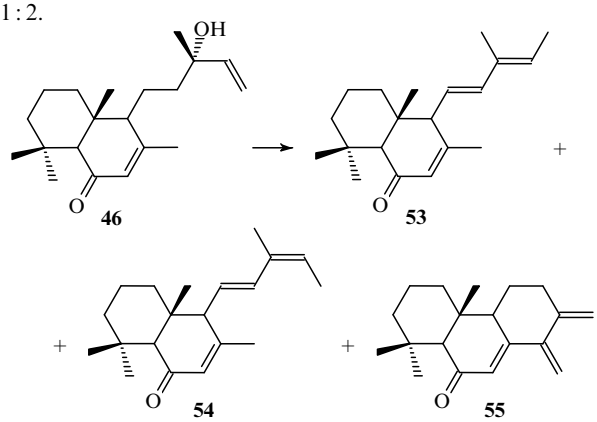
When epimanool **42** was kept on a zeolite (40 °C, 4.5 h), $\Delta^{8,9}$-pimaradiene **43** and $\Delta^{8,9}$-isopimaradiene **44** were isolated from the reaction mixture.



The transformations of 6-oxolarixol **45** on a zeolite gave bicyclic products **51** and **52**, in addition to tricyclic compounds **47–50**. The bicyclic compounds could have formed *via* the migration of the 8,17-double bond to the position conjugated with the oxo-group, which makes cyclisation impossible.



Keeping compound **46**, the $\Delta^{7,8}$-isomer of the oxoalcohol **45**, on a zeolite leads to a mixture of products containing isomeric bicyclic ketones **53** and **54** and tricyclic ketone **55** in a ratio of 2 : 1 : 2.



Analysis of experimental data permitted the researchers cited[22] to conclude that the transformations of the alcohols **42**, **45** and **46** on HY zeolite follow different pathways depending on the position of the double bond in ring *B*. In the case of the compounds **42** and **45** containing *exo*-methylene double bonds, acid-catalysed cyclisation yielding isomeric tricyclic diterpenoids occurs predominantly, whereas in the case of the compound **46** containing no highly reactive exocyclic double bond, the dehydration and polymerisation processes predominate.

A large number of works have been devoted to heterophase isomerisation of epoxides of the terpene series, which are fairly reactive compounds capable of being functionalised to alcohols, aldehydes and ketones.

Analysis of the data presented in Table 1 leads to the following conclusions. Firstly, in the presence of solid catalysts, apart from the cleavage of the epoxide ring and functionalisation of the substrate (for example, the transformations **60→61**; **62→63+64**; **87→88**), isomerisation of the carbon skeleton occurs (for example, **62 → 66**; **67→68+72**; **84→85**). Secondly, the use of various types of solid catalysts permits selective preparation from the same epoxide of products belonging to various classes. For example, limonene epoxide **62** can be converted either into ketone **61** or into aldehyde **66**, and α-pinene epoxide **67** affords either campholenic aldehyde **68**, or alcohol **70**, or the ketone **63**. Thus by varying the character of the catalyst used, one can control the reaction route. Thirdly, comparison of the products obtained from the epoxides under heterogeneous conditions (Table 1) with those formed in homogeneous acid media implies that isomerisation can follow

Table 1. Isomerisation of epoxides on solid catalysts.

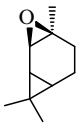
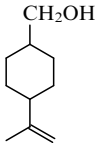
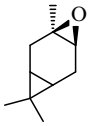
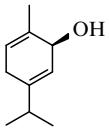
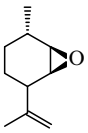
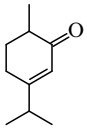
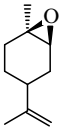
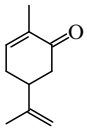
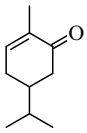
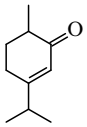
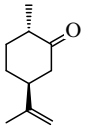
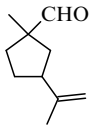
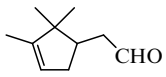
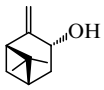
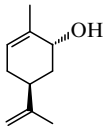
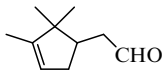
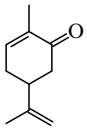
The initial epoxide	The catalyst used	The main product	Ref.
Δ^2-Carene epoxide **56** 	5A, 1010 AH, and 2020 AH zeolites	1,2-Dihydroperillic alcohol **57** 	23
Δ^3-Carene epoxide **58** 	2020 AH zeolite	2-Methyl-5-isopropylcyclo-hexa-2,5-dien-1-ol **59** 	23
Isolimonene epoxide **60** 	HSZ-360-HUA zeolite	Carvenone **61** 	23
Limonene epoxide **62** 	$ZnCl_2$/KCl/NaCl salt melt	Carvone **63** 	24
		Isohydrocarvone **64** 	
	5A and 5Ca zeolites	Carvenone **61** 	25, 26
	3A, 4A, and 13X zeolites , TSZ-645-PSH1 + + HCOOH	Dihydrocarvone **65** 	27
	3A, 4A zeolites	3-Isopropenyl-1-methyl cyclopentane-1-carb-aldehyde **66** 	28
α-Pinene epoxide **67a** 	Zeolites: HSZ-850, Na-mordenite, H-β, 3A, 4A, 13X, montmoril-lonite K-10 clay	Campholenic aldehyde **68** 	25, 29 – 32
α-Pinene epoxide **67b** 	Na-A zeolite, $NaOH/Al_2O_3$	*trans*-Pino-carveol **69** 	31, 33
	F-9 zeolite + ClCCOOH, A4 zeolite	*trans*-Carveol **70** 	28, 34
	$ZnCl_2$/KCl/NaCl salt melts	Campholenic aldehyde **68** 	24
		Pinocarvone **71** 	
	$H_2Cr_2O_4/Al_2O_3$	Carvone **63** 	34

Table 1 (continued).

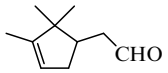
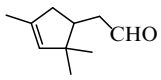
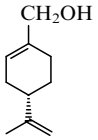
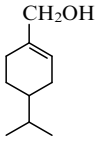
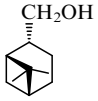
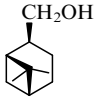
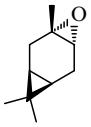
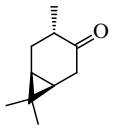
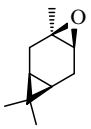
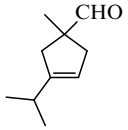
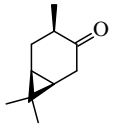
The initial epoxide	The catalyst used	The main product	Ref.
α-Pinene epoxide **67b** 	Tonsil LF-80 clay	Campholenic aldehyde **68** 	31
		Isocampholenic aldehyde **72** 	
	Al_2O_3/LiCl, Al_2O_3	Pinocamphone **73** 	32, 33
β-Pinene epoxide **74a** 	HSZ-850-NAA zeolites, ZnX_2/KX/NaX salt melts (X = Cl, Br)	*cis*-Myrtanal **75** 	24, 35
	Zeolites: 3A, 4A, 13X, TSZ-645-PSHI + HCOOH	Perillic alcohol **76** 	27, 34
	3A and 4A zeolites	Phellandrol **77** 	26
		β-Pyronene **78** 	
β-Pinene epoxide **74b** 	$NaOH/Al_2O_3$	*trans*-Myrtanol **79** 	33
	A-4 zeolite	*cis*-Myrtanol **80** 	34
trans-Epoxy-carane **81** 	Askanite – bentonite clay, β-zeolite, SiO_2	3,3,6-Trimethylbi-cyclo[3.1.0]hexane-3-carbaldehyde **82** 	36, 37
	SO_4^{2-}/ZrO_2	"	37
		trans-Caranone **83** 	
cis-Epoxy-carane **84** 	SO_4^{2-}/ZrO_2	3-Isopropyl-1-methylcyclopent-3-ene-1-carb-aldehyde **85** 	37
	SO_4^{2-}/TiO_2	*cis*-Caranone **86** 	

Table 1 (continued).

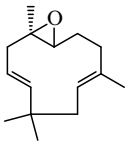
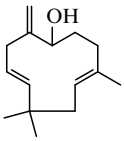
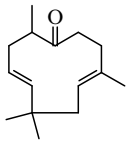
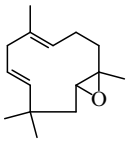
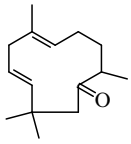
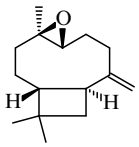
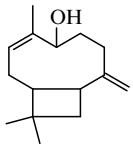
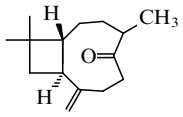
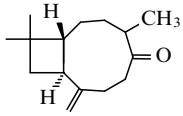
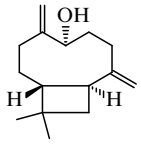
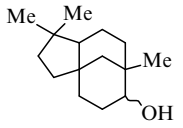
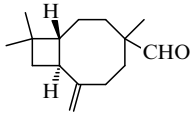
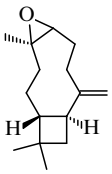
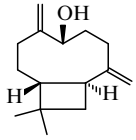
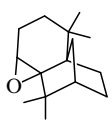
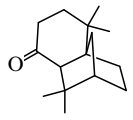
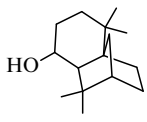
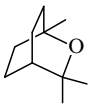
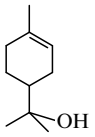
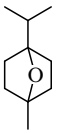
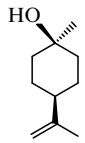
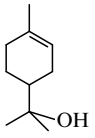
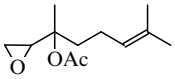
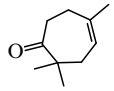
The initial epoxide		The catalyst used	The main product		Ref.
Humulene 6,7-epoxide **87**		Al_2O_3, SO_4^{2-}/Al_2O_3	Humulenol **88**		14, 38
		Askanite – bentonite clay	Humulen-7-one **89**		14
Humulene 2,3-epoxide **90**		Askanite – bentonite clay, SO_4^{2-}/ZrO_2	Humulen-2-one **91**		14
Caryophyllene 4,5-epoxide **92**		Al_2O_3	Caryophyllen-5-ol **93**		38, 39
		TSZ-320-HUA zeolite	Dihydrocaryophyllen-5-one **94**		40
		TSZ-320-HUA zeolite	Dihydroiso-caryophyllen-5-one **95**		40
		Al_2O_3	α-Betulenol **96**		39
		3A, 4A, 13X, TSZ-320-HUA zeolites	Dihydrocloven-9-ol **97**		41
		Chromosorb W	4,10,10-Trimethyl-7-methylenebicyclo[6.2.0]-decane-4-carbaldehyde **98**		42
Isocaryophyllene α-oxide **99**		Al_2O_3	β-Betulenol **100**		39
Isolongifolene epoxide **101**		3A, 4A, 13X zeolites	Isolongifolan-4-one **102**		40, 41
		"	Isolongifolan-4-ol **103**		

Table 1 (continued).

The initial epoxide	The catalyst used	The main product	Ref.
Longifolene epoxide **104** 	A-4 zeolite	Longicamphenylone **105** 	41
1,8-Cineole **106** 	Zeolites: A-4, A-5 + + HCOOH	α-Terpineol **107** 	43
1,4-Cineol **108** 	A-4 zeolite + + Cl_3CCO_2H	β-Terpineol **109** 	43
	A-4 zeolite + HCOOH	α-Terpineol **107** 	43
Linalool epoxide acetate **110** 	3A zeolite	Karahanaenone **111** 	44

different pathways under homogeneous and heterogeneous conditions. For example, the transformation of humulene 6,7-epoxide **87** in a homogeneous acid medium follows a concerted mechanism with the consecutive participation of the 9,10- and 2,3-double bonds and with fixation of the most stable *cis*–*trans*-conformation,[45] whereas on solid catalysts, the isomerisation apparently occurs by a non-concerted mechanism, and a conformation other than the most stable is fixed. Depending on the nature of the catalyst, cleavage of the epoxide ring is followed either by 1,2-hydride shift to give ketone **89** (the askanite–bentonite clay) or by abstraction of a proton yielding alcohol **88** (SO_4^{2-}/Al_2O_3).[14]

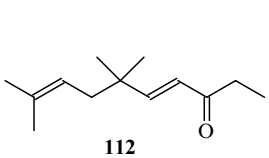
2. Photochemical isomerisation of terpenoids and their complexes with cyclodextrins

Besides thermal isomerisation of terpenoids in the presence of solid catalysts, considerable interest is aroused by photochemical transformations of these compounds; this is due to their natural origin and to the important role of solar light for the biogenetic processes.

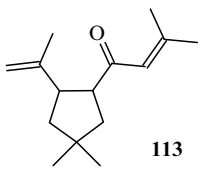
Owing to polyfunctionality and conformational flexibility of terpenoids and to the high energy of UV radiation, exposure of solutions of terpenoids to radiation usually leads to non-selective transformations yielding numerous products. To increase the selectivity of the process, complex formation is employed. The formation of complexes with cyclodextrins (CD) makes the substrates conformationally rigid by fixing a particular arrangement of the reactive sites of the molecules. Consequently, photochemical processes either occur more selectively or follow a different pathway.

Cyclodextrins are natural cyclic oligosaccharides consisting of 6 (α-CD), 7 (β-CD) or 8 (γ-CD) D-(+)-glucopyranose units linked by α-1,4-glycosidic bonds. They are capable of acting as 'hosts' in complexes of the 'host–guest' type.[2] Cyclodextrins bind a guest molecule through hydrophobic interactions, *i.e.* by forming complexes with low-polarity molecules or parts of molecules. This complex formation closely resembles binding of substrates by enzymes, which is especially valuable for the investigation of natural terpenoids. For example, complex formation with CD has been used[2,46] to change the photochemical reactivity of organic molecules. However, these studies referred only to aromatic substrates.

In a study of photochemical reactions of compounds **30a**–**c** and **112** (the latter is a homologue of the dienone **30a**), it was found[47] that on exposure to radiation, the compounds **30a**, **30c** and **112** undergo *cis*–*trans* isomerisation, while the ketone **30b** is converted into cyclopentane derivative **113**.

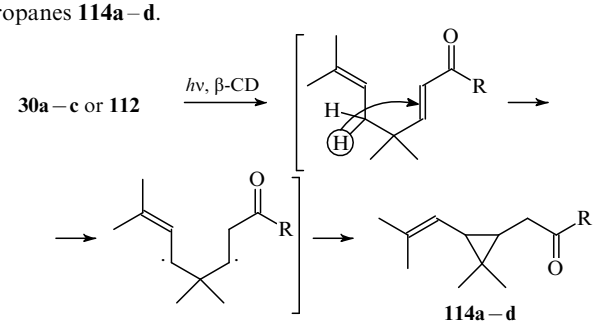


112



113

The situation changes when complexes of the ketones **30a**–**c** and **112** with β-CD are irradiated. In all the cases, the allylic hydrogen atom undergoes a 1,4-shift to the carbon atom, located in the α-position with respect to the carbonyl carbon atom, and the 1,3-biradical undergoes ring closure to give substituted cyclopropanes **114a**–**d**.



R = Me (**a**), Bu^i (**b**), $CH_2CMe=CH_2$ (**c**), Et (**d**) (**114**).

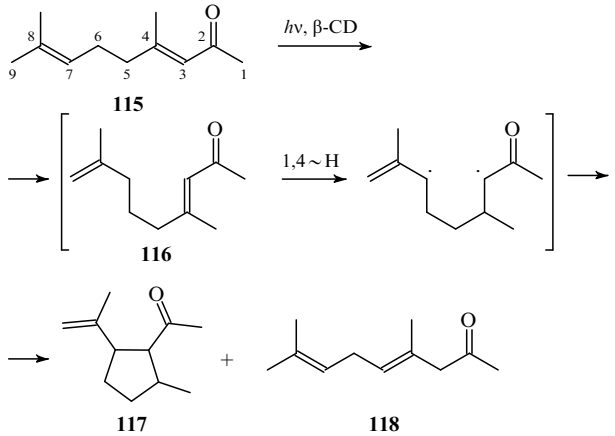
The results of the photolysis of the ketones **30a**, **30c** and **112** indicate that the size of the alkyl group R at the carbonyl carbon atom does not influence the direction of the process but does influence the yield of **114**: as the bulk of the alkyl substituent increases, the product yield decreases. Apparently, this is due to the fact that the complex formation between the substrates and β-CD becomes difficult.

Comparison of the photochemical reactions of the complexes of **30b** and **30c** with β-CD indicates that the presence of the rigid conjugated dienone system prevents the cyclisation with 1,4-shift of hydrogen yielding cyclopropanes (compound **30c**). The partial destruction of the dienone system due to allylic rearrangement facilitates transition to a conformation favourable for the cyclisation giving a cyclopropane ring.

Analysis of the products resulting from the photochemical transformations of the ketone **30b** as such and as the complex with β-CD allowed Luzina *et al.*[47] to assume that the isopropylidene group of the ketone drops into the cavity of β-CD. This assumption is consistent with the fact that the allylic rearrangement occurring on irradiation of free **30b** involves the isolated double bond, whereas irradiation of the complex results in the violation of the conjugated system of π-bonds, which is substantially less favourable energetically. The assumption that the non-conjugated double bond is shielded is also in agreement with the fact that photochemical reactions of the complexes of **30a**–**c** and **112** with β-CD are always accompanied by *trans*–*cis*-isomerisation of the double bond.

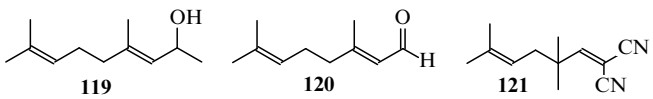
The behaviour under the same conditions of a number of compounds containing a 2,6-dimethylhepta-1,5-dienyl fragment has been studied.[21]

This seemingly insignificant modification of the structural unit results in substantial changes in the photochemical reactivity. In fact, when 4,8-dimethylnona-3,7-dien-2-one **115** is exposed to radiation, *trans*–*cis*-isomerisation of the double bond occurs. Irradiation of the complex of **115** with β-CD gives rise to cyclopentanone **117** and dienone **118** (*cf.* Refs 48 and 49).



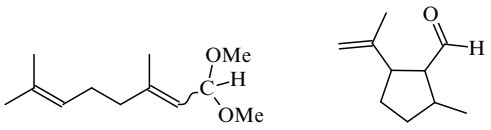
115 **116** **117** **118**

The influence of functional groups on the photochemical processes was studied[21] in relation to alcohol **119**, aldehyde **120** and nitriles **37**, **40** and **121**.



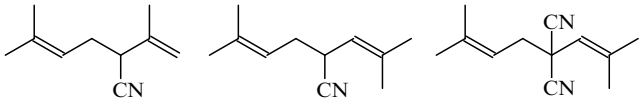
119 **120** **121**

Neither the alcohol **119** nor its complex with β-CD exhibit photochemical activity indicating that the conjugated carbonyl group plays a significant role in this process. When citral **120** in methanol is exposed to radiation in the absence of β-CD, acetal **122** is formed, while this compound bound in the complex with β-CD is converted into cyclopentanone derivative **123** (*cf.* Ref. 49).



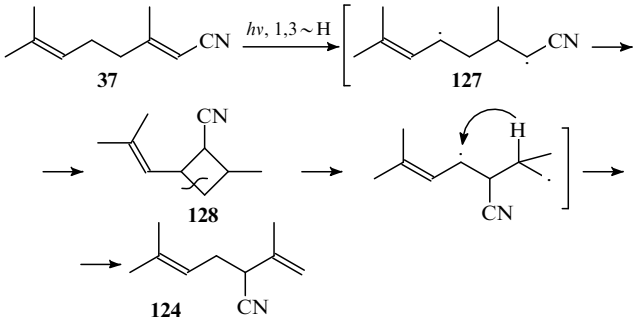
122 **123**

During irradiation of the nitriles **37**, **40** and **121**, cyclodextrin acts as a sensitiser. The reactions yield nitriles **124**–**126**, respectively.



124 **125** **126**

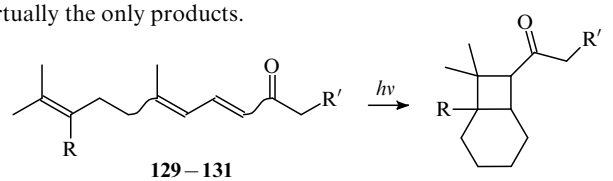
Let us consider a possible mechanism of the formation of these products using the nitrile **37** as an example.



37 **127** **128** **124**

The 1,3-hydride shift gives biradical **127**, which undergoes ring closure yielding nitrile **128** containing a cyclobutane ring. The subsequent rupture of the C–C σ-bond in the four-membered ring of the nitrile **128**, hydride shift and formation of a double bond give rise to the compound **124**.

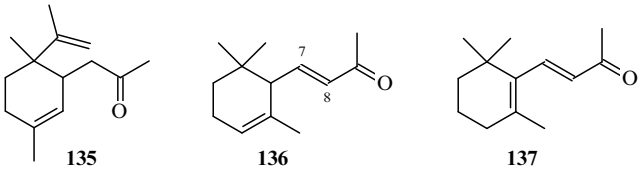
The irradiation of methanol solutions of the ketones: pseudoionone **129**, φ-irone **130** and φ-methylionone **131**, the structures of which are similar to that of the ketone **115** and the carbonyl group is conjugated with two double bonds, results in *trans*–*cis* isomerisations of both double bonds. When solutions of complexes of the ketones **129** and **131** with β-CD are exposed to radiation, bicyclic ketones **132** and **134**, respectively, are formed as virtually the only products.



129–**131** **132**–**134**

R = R′ = H (**129**, **132**); R = Me, R′ = H (**130**, **133**); R = H, R′ = Me (**131**, **134**).

Photolysis of the complex of the ketone **130** with β-CD in solution follows a different pathway: bicyclic ketone **133** and ketone **135** (~1 : 1, according to GLC) are formed as the main products.

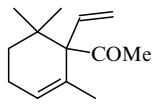


135 **136** **137**

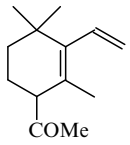
Photolysis of cyclic ionones — α-ionone **136**[21] and β-ionone **137** and products of its crotonic condensation with acetaldehyde (**138**), acetonitrile (**139**), and ethyl acetate (**140**), has been studied.[50]

The irradiation of a methanol solution of the ketone **136** and benzene solutions of the ketone **137** and the aldehyde **138** leads to

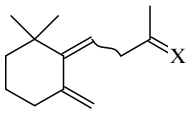
trans – cis isomerisation of the double bond. When the complex of **136** with β-CD is exposed to radiation, rearrangement products **141** and **142** are formed (~2 : 1, according to GLC), while in the case of complexes derived from **137** and **138**, retro-γ-ionone **143** and retro-γ-ionylidenacetaldehyde **144**, respectively, are formed as the major products.



141

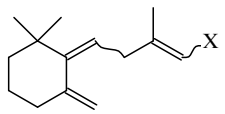


142

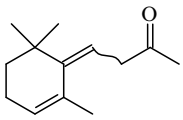


143 (X = O),
144 (X = CHCHO)

When β-ionylideneacetonitrile **139** and ethyl β-ionylideneacetate **140** are bound in complexes with β-CD, their reactivity does not change. Both these compounds themselves and their complexes with β-CD react to give compounds **145** and **146** as the main products.



145 (X = CN),
146 (X = CO_2Et).



147

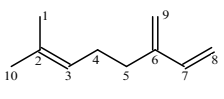
If the ketone **136** is bound in a complex with α-CD, this reaction yields retro-α-ionones **147**, instead of the compounds **141** and **142**.[21]

III. Intermolecular reactions

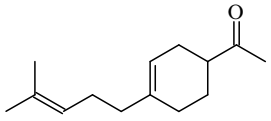
Intermolecular reactions of terpenoids in 'organised media' are of interest for both theoretical and applied organic chemistry. Multisite adsorption of reactants and substrates on solid catalysts sharply decreases the activation barriers to a number of transformations, and hence, some practically valuable processes can be conducted at low temperatures and under atmospheric pressure. The fact that the adsorbed substrate and reagent molecules can approach each other and the presence of channels and pores in the catalyst not only decrease the activation energies of the possible processes but also provide the possibility of making a reaction follow selectively a particular pathway. This pathway is often unusual and unknown in the chemistry of homogeneous reactions. The use of solid catalysts (mostly aluminosilicates) in the chemistry of terpenoids leads sometimes to results that can change our views on the role of homology, isomerism and similarity of molecules.

1. Cycloaddition reactions

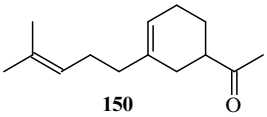
Among cycloaddition reactions involving terpenoids, a special place belongs to the Diels – Alder reaction, because the adducts that are formed are used as perfumes or intermediates for their production. To carry out reactions of this type without a catalyst, high temperatures and elevated pressures are needed. Consequently, the reaction mixtures can contain substantial amounts of resins.[51] The use of zeolite catalysts[52] or chromatographic sorbents[53] in the reactions of a natural terpene, myrcene **148**, with methyl vinyl ketone and acrolein results in the formation of Diels – Alder adducts **149** – **151** in good yields under mild conditions.



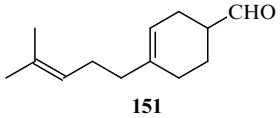
148



149



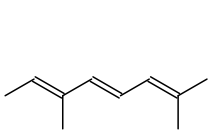
150



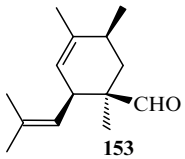
151

The $Cu^{2+}NaY$, NiNaX and dealuminised NiNaY′ zeolites and natural clinoptilolite were used as catalysts in this reaction.[52] It was found that the process is best performed without a solvent, at 50 °C using 1.5 moles of methyl vinyl ketone per mole of the triene **148** and 100% (by mass) of the NiNaX zeolite with respect to the organic components introduced in the reaction. Under these conditions, the degree of conversion of the compound **148** was 80% over a period of 5 h, and the overall yield of the products **149** and **150** was 45% (the **149** : **150** ratio was 9 : 1). In the presence of the CuNaY zeolite, the yield of the adducts **149** and **150** did not exceed 40%, their ratio being the same. The activity of natural clinoptilolite was the same as that of the NiNaX zeolite. When the reactions of the triene **148** with methyl vinyl ketone and with acrolein were carried out on the surface of a chromatographic adsorbent without a solvent, the reaction temperature could be decreased by 50 – 100 °C, and the adducts **149** and **151** were formed in good yields (73% and 66%, respectively).[53] The best effect was achieved when various kinds of silica gel for chromatography were used as the 'dry media'. Magnesium silicate was less active, and alumina was ineffective in this reaction. The catalytic effect of the sorbents was explained by the fact that the reactants, being adsorbed on them, lose their solvation shells, and this markedly facilitates the formation of pre-reaction complexes due to weak van der Waals interactions of the substrates.

The possibility of stereoselective diene condensation of alloocimene **152** with α-methylacrolein in the presence of wide-pore β-zeolite has been demonstrated.[54]



152

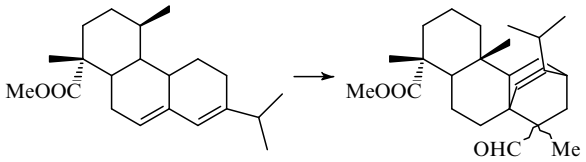


153

One of the four possible diastereomers, aldehyde **153**, is formed predominantly. Furthermore, it was found that other diastereomers do not isomerise into the compound **153** under the reaction conditions.

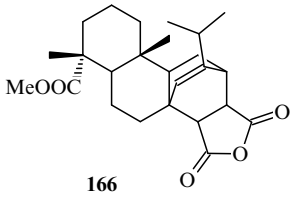
The results of the reactions of the trienes **148** and **152** with acrolein, methyl vinyl ketone, α-methylacrolein and crotonaldehyde on β-zeolite are presented in Table 2.

When the methyl ester of abietic ester **164** has been made to react with α-methylacrolein in the presence of wide-pore β-zeolite or askanite – bentonite clay (boiling benzene, 7 h), epimeric products of the Diels – Alder condensation **165a,b** have been isolated.[55]



164 **165a**,**b**

The reaction of the ester **164** with maleic anhydride on the same catalysts results in the formation of adduct **166**. In the absence of catalysts, the yield of the product **166** is five times lower, while the compounds **165a,b** are not formed at all.

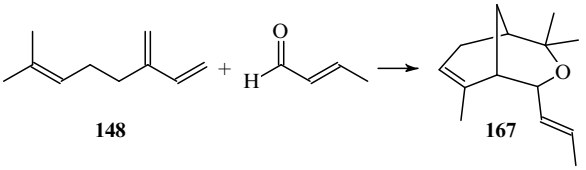


166

The reaction of the triene **148** with crotonaldehyde carried out with the askanite – bentonite clay as the catalyst unexpectedly yielded 2,2,6-trimethyl-4-(prop-1-enyl)-3-oxabicyclo[3.3.1]non-6-ene **167** as the main product.[54]

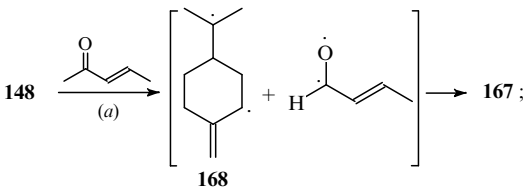
Table 2. Diels – Alder adducts obtained from the trienes **148** and **152** on a β type zeolite.[54]

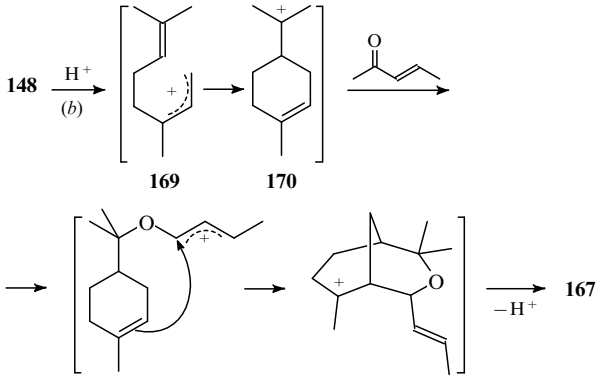
Diene	Dienophile	Adducts	Diene	Dienophile	Adducts
152	Acrolein	4,5β-Dimethyl-2β-(2-methylprop-1-enyl)-cyclohex-3-ene-1β-carbaldehyde **154**	**148**	α-Methyl-acrolein	Myrcenal **159**
		4,5β-Dimethyl-2β-(2-methylprop-1-enyl)-cyclohex-3-ene-1α-carbaldehyde **155**		Methyl vinyl ketone	Isolone **160**
	Methyl vinyl ketone	4,5β-Dimethyl-2β-(2-methylprop-1-enyl)-1β-acetylcyclohex-3-ene **156**		Croton-aldehyde	5α-Methyl-1-(4-methyl-pent-3-enyl)cyclohex--1-ene-4β-carbaldehyde **161**
		4,5β-Dimethyl-2β-(2-methylprop-1-enyl)-1α-acetylcyclohex-3-ene **157**			5β-Methyl-1-(4-methyl-pent-3-enyl)cyclohex-1-ene-4β-carbaldehyde **162**
148	Acrolein	Cyclonal **158**			4α-Methyl-1-(4-methyl-pent-3-enyl)cyclohex-1-ene-5β-carbaldehyde **163**



The formation of ether **167** is accompanied by transformation of three π-bonds into three σ-bonds and by the appearance of two new rings, *i.e.* this reaction conforms formally to the definition of the 'Diels – Alder homo-reaction'. This type of transformation is unusual, because, despite the presence of conjugated double bonds in the molecule of **148**, it involves two non-conjugated double bonds, and because α,β-unsaturated aldehyde reacts at the carbonyl group rather than at the double bond, which would be the usual pathway.

Let us dwell on the possible mechanisms of this unusual transformation. The researchers [54] proposed two mechanisms — homolytic (*a*) and heterolytic (*b*) mechanisms.

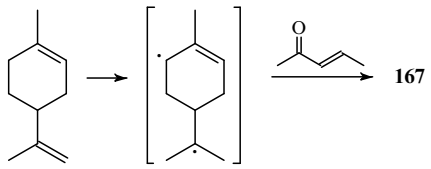




Both proposed mechanisms include the intermediate formation of compounds **168** and **170** with the *p*-menthane skeleton.

The same bicyclic ether **167** is formed in the reaction of diene **171** with crotonaldehyde. However, this reaction does not conform to the definition of Diels – Alder synthesis, because the diene **171** contains no conjugated double bonds, or to the definition of the Diels – Alder homo-reaction, since in this case only two double bonds disappear.

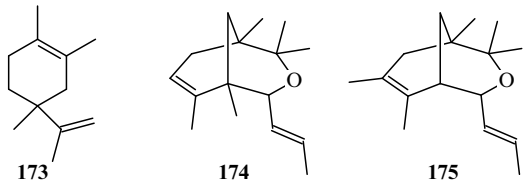
Since the formation of bicyclic ethers is of interest by itself, its mechanism has been studied in relation to the reaction of the diene **171** with various aldehydes. If the reaction of dipentene with crotonaldehyde occurs by the homolytic mechanism, one must assume that it involves the cleavage of the C(7) = C(8) double bond followed by hydride shifts to give the intermediate species **172**.



171 172

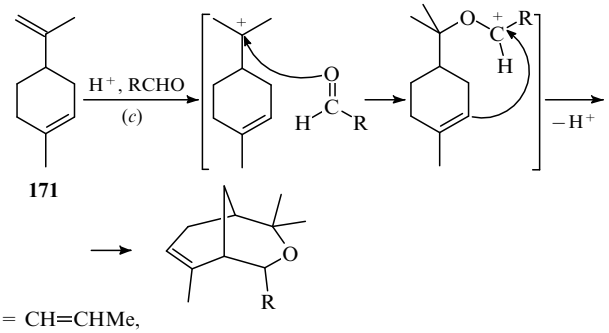
If the reaction follows the heterolytic mechanism, there is no need for the hydride shifts.

To make the choice in favour of a particular mechanism, a model compound, 4-isopropenyl-1,2,4-trimethylcyclohex-1-ene **173**, was introduced in the reaction with crotonaldehyde. The methyl group in the 4-position of this compound precludes the 1,2-hydride shifts leading to an intermediate structure like **172**. The reaction of the diene **173** with crotonaldehyde in the presence of the askanite – bentonite clay gave ether **174**; the positions of the methyl groups in this compound differ from those in compound **175**, which would have formed by the homolytic reaction route.



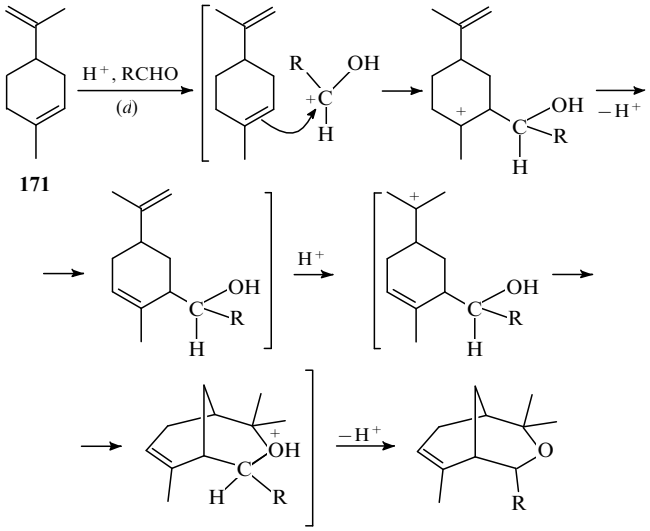
173 174 175

These facts count in favour of the heterolytic mechanism. The latter can be accomplished by two pathways.



171

R = CH=CHMe,

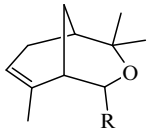


171

R = CH=CHMe.

According to the first variant (pathway *c*), the protonated diene acts as the attacking species and the aldehyde acts as a nucleophile, whereas in the second variant (pathway *d*), the protonated aldehyde is an electrophilic species and the diene acts as a nucleophile. In our opinion, the fact that the reaction of 1-methylcyclohexene with crotonaldehyde, which models the first step of pathway *d*, does not occur is evidence supporting the former pathway.

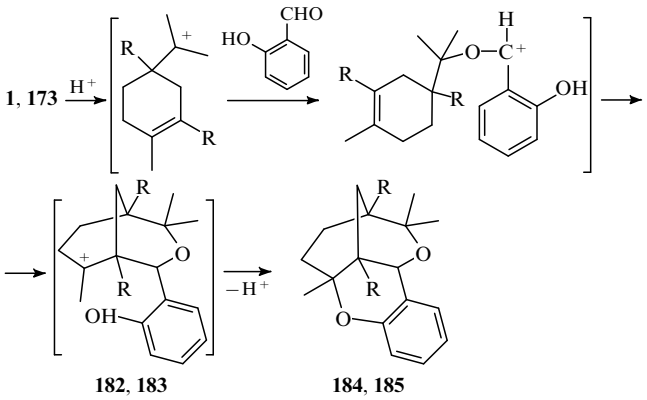
The reaction under consideration is general. Acrolein, α-methylacrolein, butyraldehyde, benzaldehyde, perfluorobenzaldehyde, and *p*-hydroxybenzaldehyde react with the diene **1** to give bicyclic ethers **176** – **181**, respectively.



176 – **181**

R = CH=CH$_2$ (**176**), MeC=CH$_2$ (**177**), Pr^n (**178**), Ph (**179**), C$_6$F$_5$ (**180**), *p*-HOC$_6$H$_4$ (**181**).

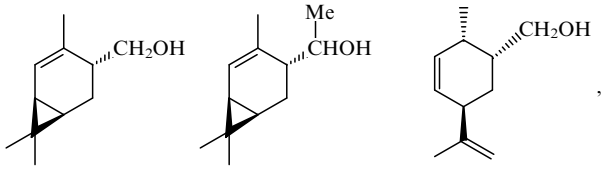
The formation of optically active ester **181** ($[\alpha]_{580}^{20} = +171.4°$, *c* 5.49, $CHCl_3$) in the reaction of the diene **1** with *p*-hydroxybenzaldehyde also supports the heterolytic mechanism for this process.[56] At the same time, the reactions of the dienes **1** and **173** with salicylaldehyde, isomeric to *p*-hydroxybenzaldehyde, on the askanite – bentonite clay at room temperature do not stop at the stage of the formation of bicyclic ethers but proceed further to give compounds with the xanthene skeleton. Thus the interaction of the cationic centre in the intermediates **182** and **183** with the *o*-OH group gives rise to 2,2,8-trimethyl-3,7-dioxa-5,6-benzotricyclo[6.2.2.0^{4,12}]dodecane **184** and 1,2,2,8,12-pentamethyl-3,7-dioxa-5,6-benzotricyclo[6.2.2.0^{4,12}]dodecane **185**, respectively.[56]



182, **183** **184**, **185**

R = H (**1**, **182**, **184**); Me (**173**, **183**, **185**).

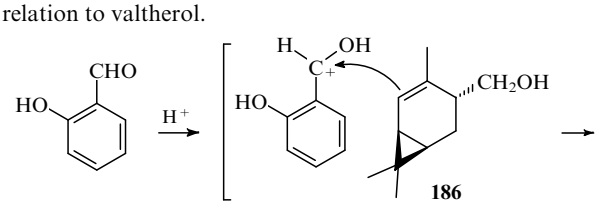
When salicylaldehyde was made to react with hydroxyalkenes of the carane and menthane series: valtherol **186**, *trans*-4-(1-hydroxyethyl)-2-carene **187** and (1*S*,4*R*,6*R*)-6-hydroxymethyl-*p*-mentha-2,8(9)-diene **188**



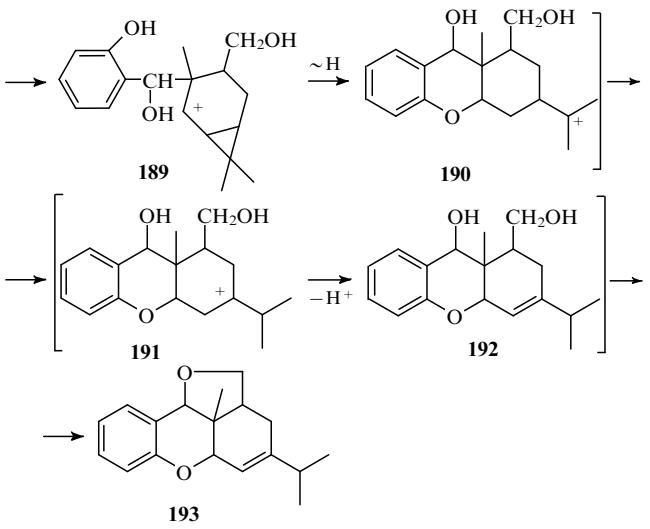
186 **187** **188**

on the askanite – bentonite clay, products with the xanthene skeleton were also obtained, but in this case, this skeleton was fused to a tetrahydrofuran ring rather than to a tetrahydropyran ring as in **184** and **185**, and the arrangement of alkyl substituents was also different.

It is clear that in this case the process follows a different pathway.[57] A possible mechanism for this reaction is shown below in relation to valtherol.

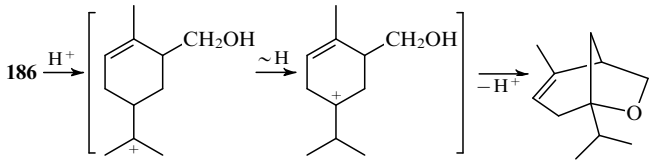


186

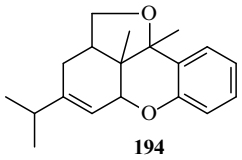


In the first step, protonated salicylaldehyde attacks the double bond of valtherol to give cation **189**. Intramolecular heterocyclisation in this cation accompanied by cleavage of the three-membered ring yields cation **190**. This can be followed by 1,2-hydride shift and deprotonation affording intermediates **191** and **192** and by heterocyclisation leading to the final product, 10-isopropyl-12-methyl-2,6-dioxa-3,4-benzotricyclo[6.3.1.0^{5,12}]-dodec-10-ene (**193**). The reactions of unsaturated alcohols **187** and **188** with salicylaldehyde apparently occur in a similar way.

A study of the behaviour of the unsaturated alcohols **186**–**188** in superacid media has shown [58] that under these conditions, the alcohols undergo intramolecular cyclisation yielding ethers with the oxabicyclo[3.2.1]octane skeleton.



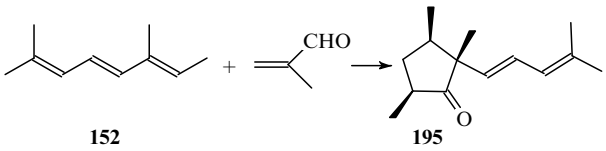
The researchers [58] suggested that the intramolecular cyclisation occurs upon the interaction of the carbocation centre with the hydroxyl group acting as an inherent nucleophile. When the reaction is carried out in the presence of the askanite–bentonite clay, the intramolecular cyclisation product of this type is formed only in the case of **187**, despite the fact that the entropy factor is favourable for this process. Apart from compound **194**, 1-isopropyl-4,6-dimethyl-7-oxabicyclo[3.2.1]oct-3-ene was isolated from the reaction mixture.[57] In other cases where the askanite–bentonite clay has been used, bimolecular reactions predominate.



194

Comparison of the reactions of salicylaldehyde with the dienes **1** and **173** and with the unsaturated alcohols **186**–**188** shows that, although both processes afford xanthene derivatives, in the former case the protonated diene acts as an electrophile and the aldehyde is a nucleophile, while in the latter case, the protonated aldehyde reacts as an electrophile and the unsaturated alcohol is a nucleophile.

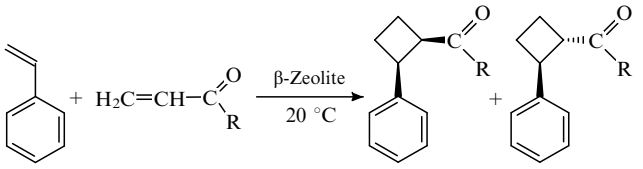
Interesting results have been obtained when alkenes have been made to react with compounds containing a vinyl or vinylidene group. An unusual reaction of the triene **152** with α-methylacrolein on the wide-pore β-zeolite has been reported.[54] The reaction occurs stereoselectively and yields substituted cyclopentanone **195**.



152 **195**

It is noteworthy that this reaction, which can formally be regarded as [3 + 2]-carbocyclisation with a 1,2-shift of the aldehyde proton, involves only one of the three double bonds of the triene **152**, while the two other bonds are incorporated unchanged in the ketone **195**. This fact stimulated Tatarova *et al.*[59] to search for monoalkenes that would enter into the same unusual reaction with α-methylacrolein. They found that of a broad range of alkenes including terpenes and model compounds, only styrene reacted with α-methylacrolein (β-zeolite, 20 °C). This reaction yields a mixture of diastereomers of 5-methyl-2-phenylcyclopentanone **196**.

This process, like the reaction of α-methylacrolein with the triene **152**, occurs as [3 + 2]-carbocyclisation accompanied by a 1,2-shift of the aldehyde hydrogen atom. The reactions of styrene with methyl vinyl ketone and acrolein in the presence of the wide-pore β-zeolite result unexpectedly in the formation of cyclobutane derivatives **197**–**200**.[59]

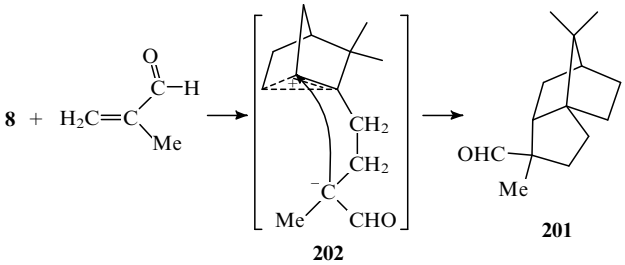


197, 198 **199, 200**

R = Me (**197**, **199**), H (**198**, **200**).

These reactions are among the best studied processes in the chemistry of photochemical transformations of unsaturated compounds and are referred to as 'cyclobutane reactions'. It is noteworthy that the formation of [2 + 2]-cycloaddition products from non-activated (or weakly activated) alkenes at room temperature is quite unusual. Thermal [2 + 2]-cycloaddition also occurs fairly rarely and is observed, as a rule, on prolonged heating of acetylene derivatives [60] or perhalogenated ethene derivatives.[61]

When α-methylacrolein reacts with camphene **8** which, like styrene, contains a terminal double bond but attached to the bicyclic framework, a cyclopentane fragment does form; however, the reaction pathway differs from that in the case of the triene **152**.[59] This reaction is accompanied by the rearrangement of the bicyclic skeleton and gives 4,10,10-trimethyltricyclo-[5.2.1.0^{1,5}]decane-4-carbaldehyde **201**.

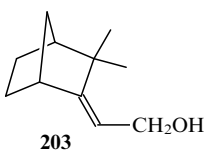


202 **201**

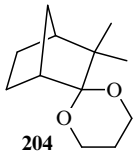
In this case, intermediate **202** is formed initially. Intramolecular stabilisation of the cationic centre results in a new carbocycle with an aldehyde group in the side chain.

The common feature of the reactions of α-methylacrolein with the compounds **152** and **8** is that [3 + 2]-carbocyclisation does occur in both cases. However, in the former case, it results from the transfer of a hydrogen atom, while in the latter case, it is due to the charge transfer. In the former case, the alkene acts as a dienophile and the aldehyde acts as a '1,3-dipole', while in the latter case, the aldehyde is a dienophile and the alkene is the '1,3-dipole' precursor.

Now we consider the reaction of camphene **8** with formaldehyde on the wide-pore β-zeolite. The condensation of these compounds in the presence of acid catalysts (the Prins reaction)[62] or in the presence of the KU-2 cation-exchange resin[63] yields mostly products with the non-rearranged camphene skeleton, namely 8-hydroxymethylcamphene **203** (or its ethers) and 1,3-dioxane **204**.

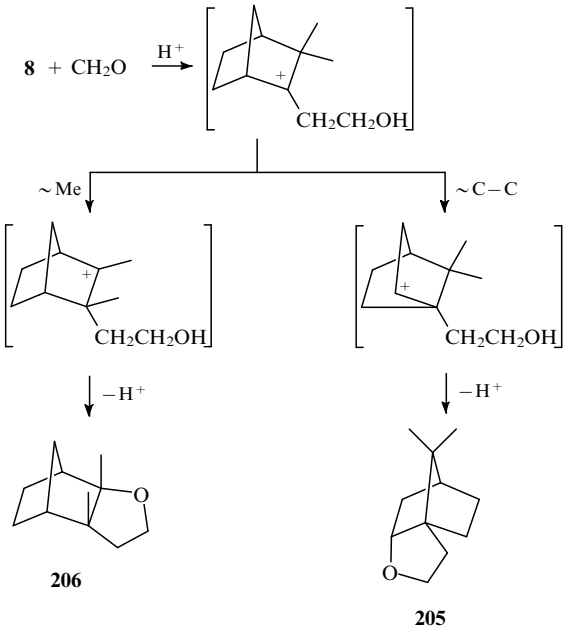


203



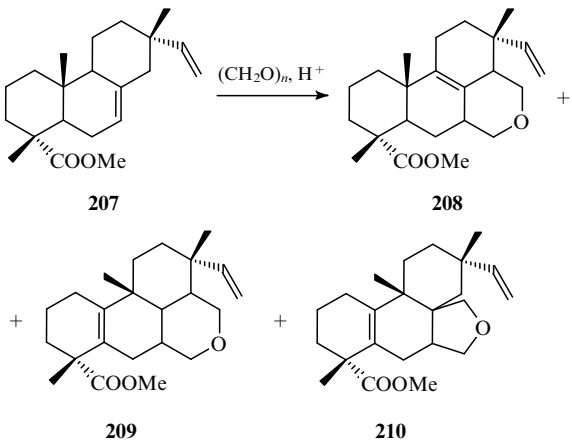
204

When this process is carried out on the β-zeolite, the formation of unusual products — tricyclic ethers **205** and **206** — becomes the main reaction pathway.[59] In the first stage, a protonated formaldehyde molecule attacks the C = C double bond in the compound **8**, and then the reaction follows two pathways: (1) Wagner – Meerwein rearrangement in which the positive charge is stabilised via binding to the oxygen atom (ether **205**); (2) 1,2-shift of the *exo*-methyl group followed by stabilisation of the arising cation (ether **206**).



206 **205**

A different variant of the Prins reaction, which is also unusual, is accomplished when methyl isopimarate **207** reacts with paraformaldehyde on the askanite – bentonite clay.[64]



207 **208**

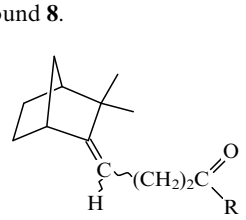
209 **210**

It was assumed that the products **208** – **210** are formed via successive addition of two equivalents of protonated formaldehyde to the initial ester **207**. The researchers noted that the reaction of the second formaldehyde molecule with the intermediate formed does not yield 1,3-dioxanes as would be the case in the classical variant of the Prins reaction or in the presence of other aluminosilicate catalysts.[1] Instead, it occurs again by the 'ene' mechanism giving rise to tetracyclic compounds with tetrahydropyran or tetrahydrofuran rings. During the reaction, 1,2-shift of the methyl group occurs, accompanied by the transformation of compounds of the pimarane series into rosane type compounds.

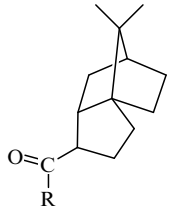
2. Addition reactions

In this Section, we consider the addition reactions in which at least the main reaction pathway is not associated with cycloaddition.

The use of other carbonyl compounds, for example, acrolein or methyl vinyl ketone in place of formaldehyde, in the reaction with the alkene **8** results in the formation of only slight amounts of carbocyclisation products **213a**,**b**. Compounds **211** and **212** formed as mixtures of geometrical isomers are the major products in this case. These compounds can formally be regarded as resulting from replacement of the vinylic hydrogen atom in compound **8**.



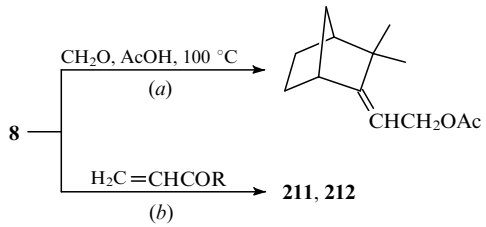
211a,**b**, **212a**,**b**



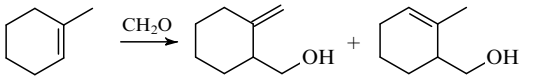
213a,**b**

R = H (**a**), Me (**b**).

Judging from the structures of the main products, the reaction under consideration resembles most closely two well known processes: the 'ene' reaction and the Prins reaction; however, it differs from these reactions in some significant points. According to the definition proposed by Snider,[65] an 'ene' reaction is the interaction of an alkene having an allylic hydrogen atom (the 'ene') with a compound containing a double or a triple bond (the 'enophile') with the formation of a new bond accompanied by the migration of the double bond in the 'ene' and by the 1,5-hydrogen shift. In the reaction under consideration, alkene **8** acts as the 'ene' having an allylic hydrogen, while acrolein or methyl vinyl ketone acts as the 'enophile'. The interaction yields two σ-bonds (C – C and C – H); no double bond migration or 1,5-shift of the allylic hydrogen occurs. Thus, the reaction in question does not conform to the definition of the 'ene' reaction. Now we compare this transformation of the alkene **8** with the Prins reaction.



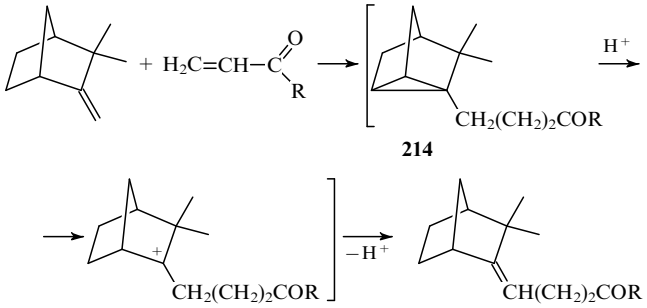
The Prins reaction (pathway *a*) consists in the interaction of a protonated aldehyde (which is H_2C^+OH virtually in all cases) with a double bond resulting in the transformation of the carbonyl group into an alcohol group or into the corresponding ether. If the reaction of an alkene with formaldehyde is carried out thermally without a catalyst, it affords products of 'ene' synthesis, for example



When carbonyl compounds are made to react with the alkene **8** in the presence of a zeolite, the β-olefinic atom attacks initially

the polarised double bond, and the carbonyl group remains intact. Thus, this process cannot be classified as the Prins reaction. This type of reaction could be referred to as 'pseudo-ene synthesis'.

Now we consider a possible mechanism of the 'pseudo-ene synthesis'. For example, the process can occur as a sequence of transformations with the intermediate formation of tricyclic derivative **214**.

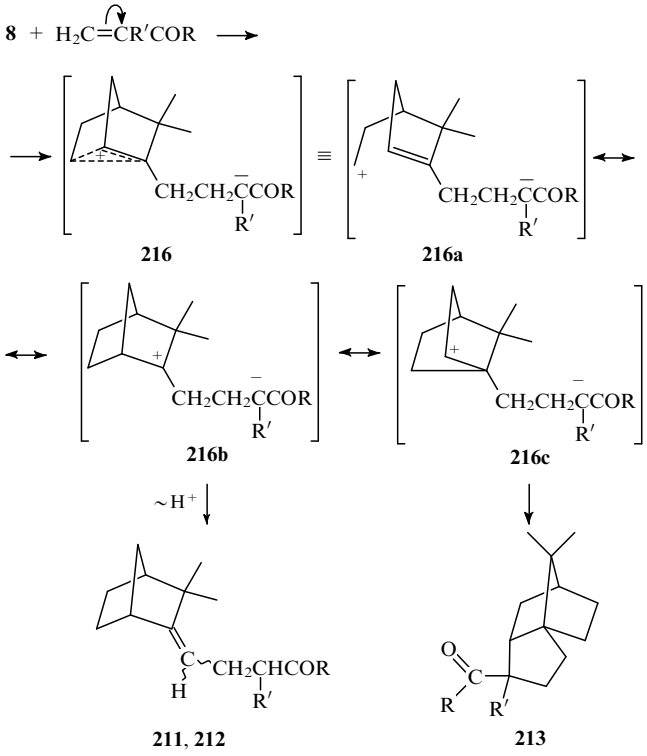


R = H, Me.

Reactions of this type have been reported previously;[66] however, the tricyclic product described in this study was converted into a bicyclic compound only on refluxing in AcOH.

Thus if we assume that the reaction occurs via the intermediate **214**, we should expect the formation of tricyclic products. However, this is not the case.

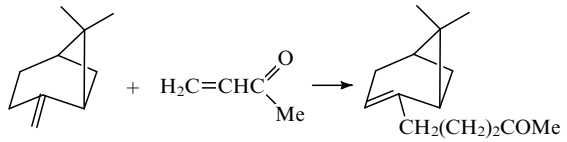
Probably, the reaction under consideration occurs via the intermediate formation of non-classical ion **216**:



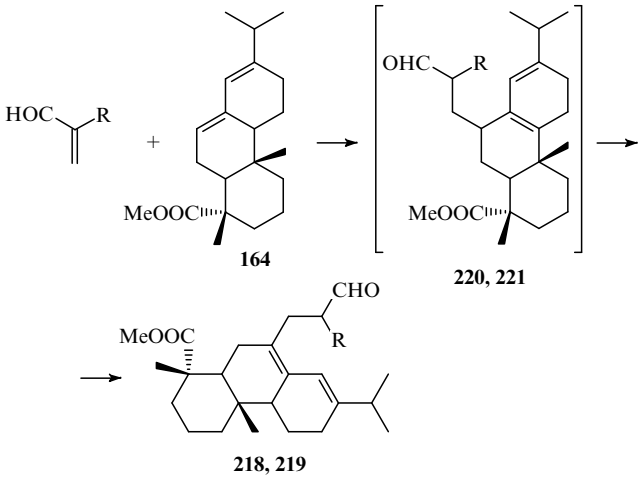
R = R′ = H (**a**), R = Me, R′ = H (**b**). R = H, R′ = Me.

This ion can be represented as the set of resonance structures **216a**–**216c**, which can undergo either carbocyclisation (**216c**→**213**) or formation of a double bond (**216b**→**211**, **212**). The relationship between these routes is governed by the nature of the substituent R′.

When aluminosilicate catalysts are used in reactions of enophiles with alkenes in which the allylic hydrogen atom is more mobile than that in **8**, typical products of the 'ene' reaction are formed. For example, it has been reported[59] that the reaction of alkene **7** with methyl vinyl ketone on the β-zeolite gives rise to 6,6-dimethyl-2-(4-oxopentyl)bicyclo[3.1.1]hept-2-ene **217**.

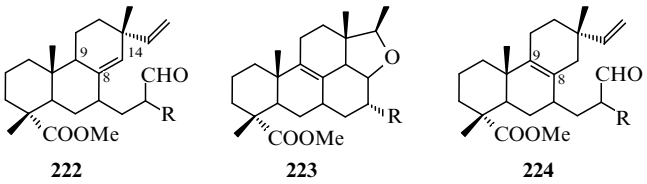


The reaction of the compound **164** with acrolein or α-methylacrolein in the presence of the β-zeolite gives compounds **218** and **219**, which result from isomerisation of the products of the ene synthesis **220** and **221**.[55]



R = H (**218**, **220**), Me (**219**, **221**).

Methyl isopimarate **207** containing one endocyclic C = C bond and two allylic hydrogen atoms in the 9- and 14-positions reacts with acrolein or α-methylacrolein in the presence of the β-zeolite or askanite–bentonite clay according to two competing pathways: $\Delta^{8,9}$- and $\Delta^{8,14}$-ene condensation,[67] the latter being the predominant pathway. Under the reaction conditions, the product of $\Delta^{8,14}$-condensation **222** undergoes further transformations, namely, intramolecular reaction of the aldehyde group with the double bond followed by cyclisation of the resulting alcohol to ether **223** with a new type of skeleton. The product of $\Delta^{8,9}$-condensation **224** is more stable under the reaction conditions and undergoes no secondary transformations, although it is formed in substantially smaller amounts.

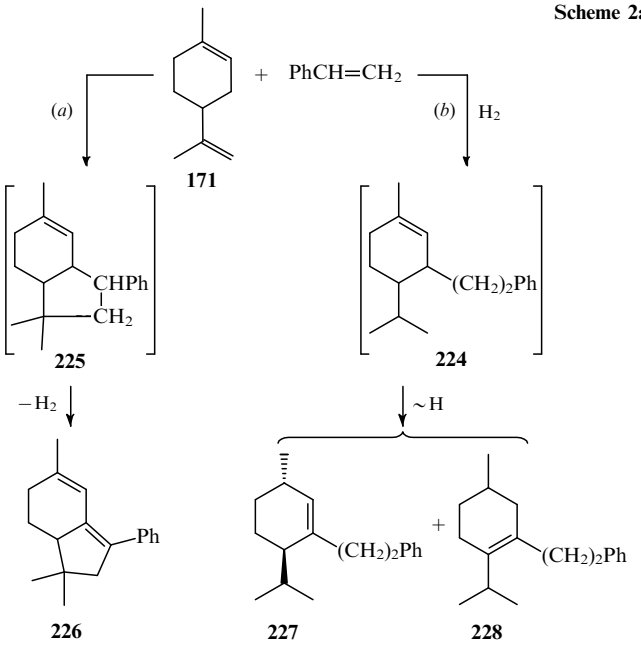


R = H, Me.

Interesting results have been obtained when styrene has been involved in the reaction with the terpenes **171** and **5**, containing no carbonyl group, on the askanite–bentonite clay. The reaction of the diene **171** with styrene at room temperature leads to a mixture of products **226**, **227** and **228** in a ratio of 1.5 : 1 : 3 (Scheme 2a).

The bicyclic compound **226** is probably formed via dehydrogenation of the intermediate **225**, which can be formally regarded as resulting from [3C + 2C]-cycloaddition. The compounds **227** and **228** can be regarded as the products of alkylation and hydrogenation of **171** to give the intermediate **224** which then

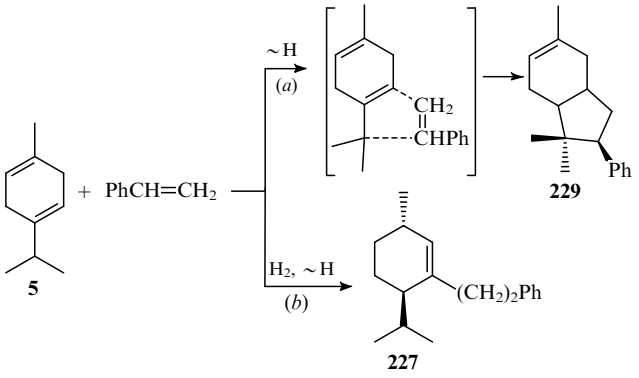
Scheme 2a



undergoes allylic rearrangements. The workers [59] have noted that in the presence of clay, the diene **171** does not react with styrene derivatives containing electron-withdrawing (*p*-nitrostyrene, *p*-bromostyrene, 2,3,4,5,6-pentafluorostyrene) or electron-donating (*p*-methylstyrene) substituents. Apparently, the influence of substituents is mostly due to the steric restrictions to the adsorption of the substrate on a catalyst created by them rather than by their electronic effects.

The interaction of styrene with the diene **5** also affords a mixture of products: alkene **228**, bicyclic compound **229** and *p*-cymene (Scheme 2b). It is noteworthy that that the mode of coupling of the molecules of styrene and **5** giving rise to compound **229** differs from that leading to the product **226**.

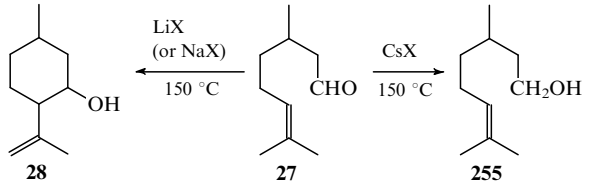
Scheme 2b



It is also noteworthy that the processes of hydrogenation and dehydrogenation of the alkenes **171** and **5** occur at room temperature. In fact, hydrogenation of alkenes is usually carried out in the presence of zeolite catalysts doped with metals such as Pt, Pd or Ru at 100–200 °C, while dehydrogenation is performed with the same catalysts at 400–600 °C.[1]

Considerable attention of researchers has been paid to the hydration of terpenoids with various hydroxyl-containing reagents on aluminosilicate catalysts. The catalysts used for this purpose and the products thus obtained are listed in Table 3. Analysis of the results of these reactions indicates that hydration of terpenoids is accompanied by rearrangements, by oxidation of the alcohols formed initially and by the formation of ethers from these alcohols.

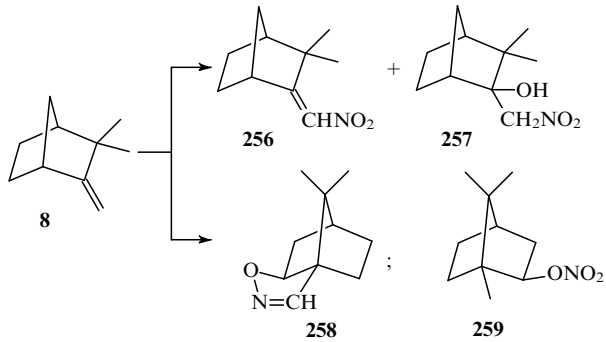
Replacement of the aluminium alkoxide in the Meerwein–Ponndorf–Verley reaction by zeolites leads to reduction of the aldehyde **27** either to the cyclic alcohol **28** or to acyclic citronellol **255**, depending on the catalyst used.[77]



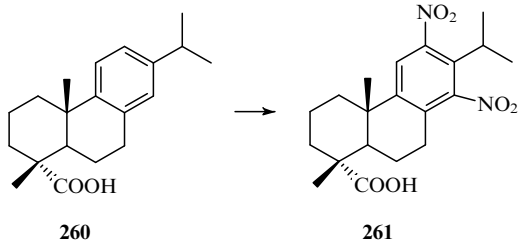
However, in the presence of zeolites, **27** cyclises to **28** (see Ref. 18) and, in all probability, it is more correct to regard this reaction, carried under the conditions described,[77] as carbocationic cyclisation rather than as the Meerwein–Ponndorf–Verley reaction.

The nitration of camphene **8** with N_2O_4 or with 69% HNO_3 in the presence of various zeolite catalysts has been studied.[78]

It was shown [78] that when N_2O_4 is used, depending on whether or not a catalyst is present and on the type of the solvent, the reaction occurs either as nitration to give ω-nitrocamphene and 2-hydroxy-3,3-dimethyl-2-nitromethylnorbornane **257** or as nitrosation followed by rearrangement of the camphene skeleton and by intramolecular cyclisation yielding 10,10-dimethyl-3-aza-4-oxatricyclo[5.2.1.$0^{1,5}$]dec-2-ene **258**. Variation of the nature of the zeolite basically does not change the reaction outcome. When camphene **8** reacts with 69% HNO_3, isobornyl nitrate **259** is formed as the major product; the addition of a zeolite has virtually no influence on the composition of the reaction mixture.

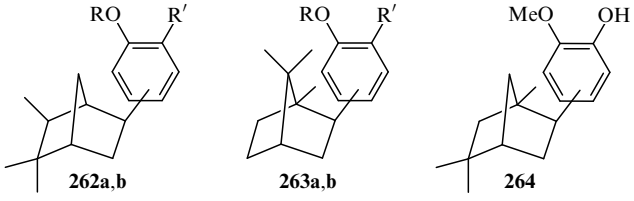


The nitration of dehydroabietic acid **260** in the presence of acidic montmorillonite impregnated with copper nitrate affords 12,14-dinitrodehydroabietic acid **261** in a good yield.[79]



Now we consider arylation and alkoxylation of terpenoids on aluminosilicate catalysts. This group of reactions is very significant, because many of the products obtained in this way are used as intermediates for the production of perfumes.[80]

When camphene **8** is arylated with phenols using the askanite clay as the catalyst, the composition of the reaction mixture depends on the reaction temperature.[81] At 160–180 °C, the mixture consists only of terpenophenols **262**–**264**.



R = R′ = H (**a**); R = Me , R′ = OH (**b**).

Table 3. Hydration of terpenoids on solid catalysts.

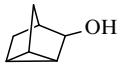
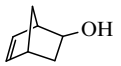
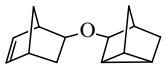
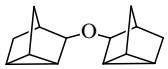
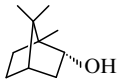
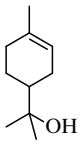
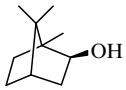
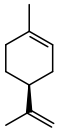
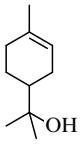
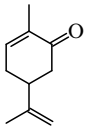
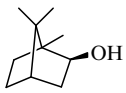
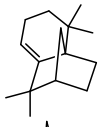
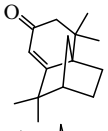
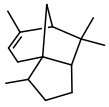
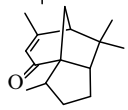
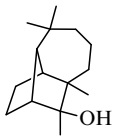
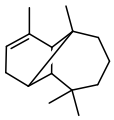
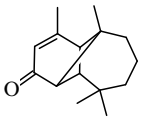
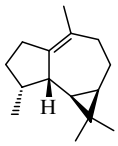
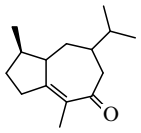
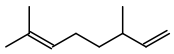
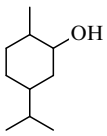
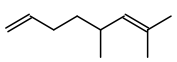
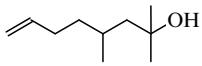
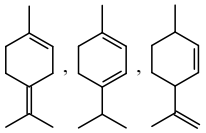
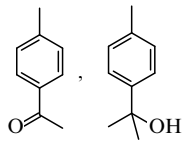
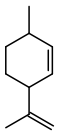
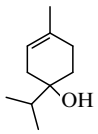
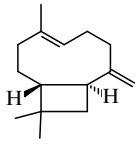
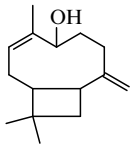
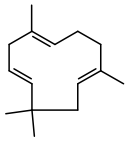
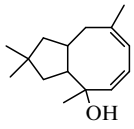
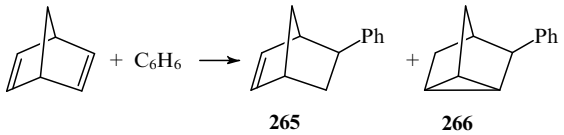
Terpenoid	The catalyst used	Reaction products	Ref.
Norbornadiene **230** 	H-Ultrasil	Nortricyclen-3-ol **231** 	68
		5-*exo*-Hydroxynorborn-2-ene **232** 	
	NdNaY zeolite	Ether **233** 	68
		Ether **234** 	
α-Pinene **6** 	GO-82 zeolite	Borneol **235a** 	69
	3A, 4A, 13X zeolites + $Al(OH)_3$, HSZ-710-HOA	α-Terpineol **107** 	70, 75
β-Pinene **7** 	2020AM zeolite	*trans*-Verbenol **236** 	70
Camphene **8** 	HSZ-600-HOA zeolite + $CuCl_2$	Isoborneol **235b** 	70
Limonene **1** 	3A and 4A zeolites	α-Terpineol **107** 	70
	HSZ-710-HOA zeolite	Carvone **63** 	70
Tricyclene **237** 	HSZ-640-HOA zeolite + $Cu(OH)_2$	Isoborneol **235b** 	70
Isolongifolene **10** 	HSZ-600-HOA zeolite	9-Oxoisolongifolene **238** 	71
α-Cedrene **239** 	HSZ-600-HOA zeolite	α-Cedranone **240** 	72
Longicyclene **241** 	2020AH zeolite	Longicamphene hydrate **242** 	73
Longipinene **243** 	HSZ-600-HOA zeolite	Longiverbenone **244** 	73

Table 3 (continued).

Terpenoid	The catalyst used	Reaction products	Ref.
(+)-Ledene **14** 	Various zeolites + $Ni(OH)_2$	3-Isopropyl-6,10-dimethyl-bicyclo[5.3.0]dec-6-en-5-one **245** 	73
Dihydro-myrcene **246** 	HSZ-620-HOA zeolite + $Al(OH)_3$	Carvomenthol **247** 	74
5,7-Dimethyl-1,6-octadiene **248** 	HSZ-640-HOA zeolite + $CHCl_2COOH$	2,4-Dimethyloct-7-en-2-ol **249** 	74
Terpinolene **2**, α-Terpinene **4**, Isolimonene **250** 	HSZ-320-HOA, HSZ-600-HOA zeolites	*p*-Methylaceto-phenone **251**, 2-(*p*-Tolyl)-propan-2-ol **252** 	75
Isolimonene **250** 	HSZ-640-NAA zeolite	Terpinen-4-ol **253** 	75
Caryophyllene **21** 	3A, 4A zeolites	Caryophyllen-5-ol **93** 	
α-Humulene **11** 	H-zeolites	2,6,10,10-Tetramethylbicyclo[6.3.0]undeca-3,5-dien-2-ol **254** 	76

When the temperature is decreased to 100 °C, the reaction mixture contains up to 60% of terpenophenyl ethers. The terpenophenol fraction consists mostly of *o*-terpenophenols, the terpene residues of which have the isocamphyl structure (**262a**, 74%) or isobornyl structure (**263a**, 26%). In some studies,[81–84] in addition to the traditional acid catalysts (Lewis and Brønsted acids), the askanite clay was also used for arylation of various terpenes. In each case, a broad range of compounds have been obtained. This was explained by secondary rearrangements of labile terpene skeletons, by dearylation, and by possible attack at various positions of the aromatic ring by the arising bicyclic carbocations. For example, when the alkene **8** condenses with guaiacol, the reaction mixture contains products **264** with the isofenchyl skeleton, together with the compounds **262b** and **263b**.

Arylation of terpenes and model compounds has been carried out on zeolite catalysts. For example, phenylation of norbornadiene **230** on wide-pore and medium-pore zeolites has been described.[85]

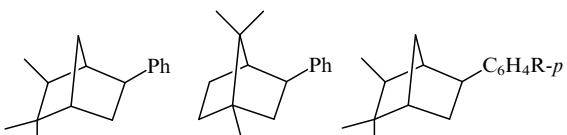


265 **266**

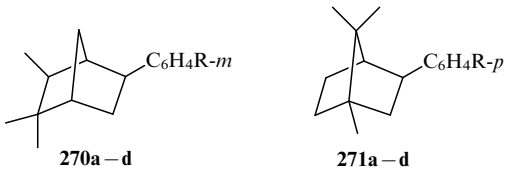
In the presence of wide-pore zeolites, 5-phenyl-2-norbornene **265** and 3-phenylnortricyclene **266** were obtained; medium-pore catalysts proved to be inactive in this reaction. Arylation of 1- and 2-methylnorbornenes with aromatic hydrocarbons in the presence of the TsEOKAR-2 zeolite-containing catalyst has been reported.[86] This reaction gave a mixture of hydrocarbons of unknown structures.

Arylation of camphene **8** with benzene and its mono- and disubstituted derivatives in the presence of the wide-pore β-zeolite has been investigated.[87]

The reaction of benzene with optically active camphene yields racemic products **267** and **268**, the former compound predominating. Attention is attracted by the unusual structure of the terpene skeleton in the compound **268** with the methyl groups at the 1-, 4-, and 7-positions. For this skeleton to be formed, at least a five-stage rearrangement of the arising camphenyl cation must occur; therefore, the researchers[87] put forward the hypothesis that the carbocations generated from camphene on zeolites possess relatively long lifetimes.



267 **268** **269a – d**

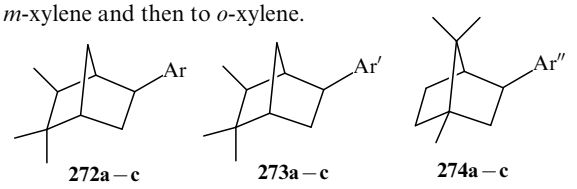


270a–d **271a–d**

R = Me (**a**), Et (**b**), Pr^n (**c**), Bu^t (**d**).

Analysis of the reaction mixtures obtained by the reaction of the alkene **8** with monoalkyl-substituted benzene derivatives indicates that as the size of the alkyl substituent increases, the overall yield of products diminishes from 60% (**269a**–**271a**) to 20% (**269d**–**271d**). The proportion of the meta-isomer **270a**–**d** in the mixture increases with an increase in the bulk of the alkyl group. Monosubstituted benzene derivatives containing electron-donating groups other than methyl (phenol, anisole) or electron-withdrawing groups (nitrobenzene, benzaldehyde, chlorobenzene) do not enter into the reaction with camphene **8** on the β-zeolite.

Isomeric xylenes give rise to products **272** – **274**, the overall yield of the reaction products increasing on passing from *p*-xylene to *m*-xylene and then to *o*-xylene.

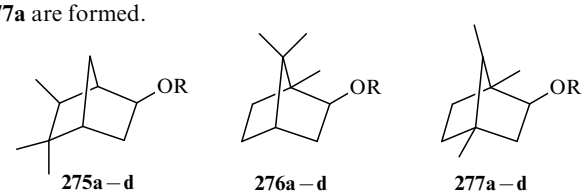


272a–c **273a–c** **274a–c**

Ar =	Ar′ =	Ar″ =
2,5-$Me_2C_6H_3$(**272a**),	2,5-$Me_2C_6H_3$(**273a**),	2,5-$Me_2C_6H_3$(**274a**),
2,4-$Me_2C_6H_3$(**272b**),	2,6-$Me_2C_6H_3$(**273b**),	2,4-$Me_2C_6H_3$(**274b**),
3,4-$Me_2C_6H_3$(**272c**)	2,3-$Me_2C_6H_3$(**273c**)	3,4-$Me_2C_6H_3$(**274c**)

Mesitylene does not react with camphene. Naphthalene and biphenyl also do not enter into this reaction, although their successful alkylation with lower alkenes in the presence of zeolites has been reported in a vast number of studies (see, for example, Ref. 88).

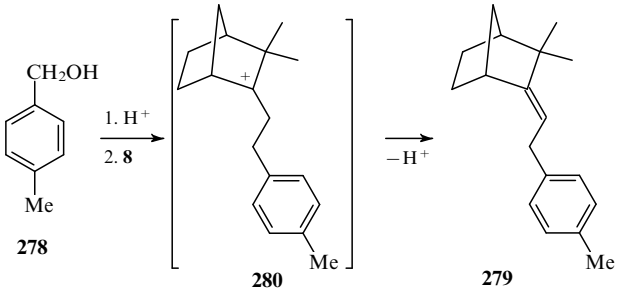
When benzyl alcohol reacts with the alkene **8** on the β-zeolite, alkoxylation occurs instead of arylation, and the ethers **275a**–**277a** are formed.



275a–d **276a–d** **277a–d**

R = CH_2Ph (**a**), CH_2CH_2Ph (**b**), $CH_2C_6H_4Me$-*m* (**c**), Me (**d**).

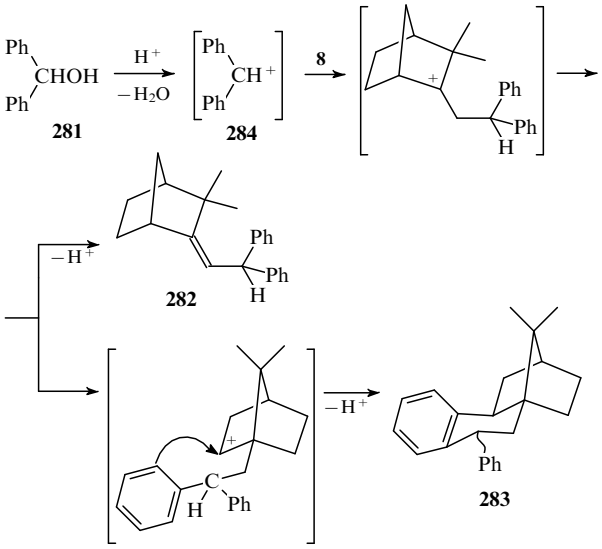
Phenethyl alcohol reacts with the alkene **8** in the presence of the β-zeolite to give the ethers **275b**–**277b**. The introduction of strong electron-donating (*p*-methoxy) or strong electron-withdrawing (*p*-nitro) substituents into the aromatic nucleus of benzyl alcohol retards alkoxylation. However, *m*-methylbenzyl alcohol is readily converted into the ethers **275c**–**277c**. The reaction involving *p*-methylbenzyl alcohol **278** requires much more rigorous conditions and follows another route yielding hydrocarbon **279**.



278 **280** **279**

The study of the reactions of camphene with *p*- and *m*-methylbenzyl alcohols showed that minor changes in the structure of the reactant result in an absolutely different reaction pattern. This fact cannot be explained by merely the different thermal effects of formation of *p*- and *m*-methylbenzyl cations from the corresponding alcohols and of the camphenyl cation from the alkene **8**, because the difference between the energies of formation of the methylbenzyl cations is relatively small.

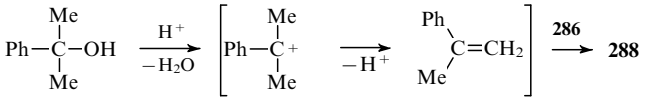
It may be expected that the transition from benzyl alcohol to benzhydrol would lead to *C*-alkylation instead of *O*-alkylation. In fact, the reaction of benzhydrol **281** with the alkene **8** yields hydrocarbons **282** and **283**.[89]



281 **284** **282** **283**

Apparently, in the reaction of the alkene **8** with the alcohol **281**, it is the benzyl cation **284** arising from the alcohol **281** upon protonation and dehydration that acts as the electrophilic species, and not the camphenyl cation, as in the reaction of **8** with benzyl alcohol or aromatic hydrocarbons. Evidently, the cation **284** is more stable than the cation **280** and, hence, the reaction of the alkene **8** with the alcohol **281** occurs under markedly milder conditions than that with the alcohol **278**. The dissimilar reaction pathways observed in the case of benzyl alcohol and benzhydrol may be due to the differences between the enthalpies of formation of the camphenyl cation, the ion **284** and the benzyl cation from the corresponding precursors; this assumption was confirmed by AM1 and PM3 calculations.[89]

α,α-Dimethylbenzyl alcohol **285**, which is also capable of forming a stable benzyl cation, apparently does form it. This cation (**286**) is then converted into α-methylstyrene **287**; the latter is more nucleophilic than the alkene **8** present in the reaction mixture and, therefore, it reacts with the cation **286** to give 1,3,3-trimethyl-1-phenylindan (**288**).

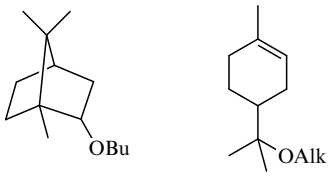


285 **286** **287**

Thus, aliphatic-aromatic alcohols, depending on their structure, can react with camphene on zeolites according to two pathways: (1) to give ethers — *O*-alkylation; (2) to give hydrocarbons with the formation of a new ring or a new linear chain — *C*-alkylation. The process yielding indane derivatives does not involve the alkene **8**.

The reaction of **8** with aliphatic alcohols, for example, with methanol, on the β-zeolite also leads to ethers (**275d**–**277d**). The preparation of the ether **276d** from **8** and methanol in the presence of the HSZ-330HUA zeolite has also been reported.[90]

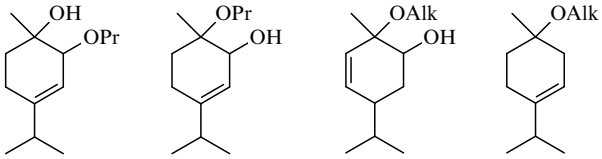
This zeolite was also used to obtain ethers **289** and **290** from tricyclene **237** and butanol and from 2- and 3-carenes and alkanols, respectively.[90]



289 **290**

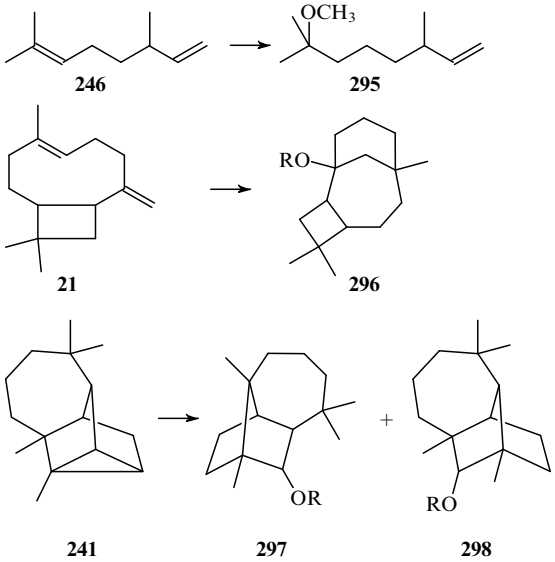
The reaction of α-terpinene **4** with propanol on the HSZ-600HOA zeolite gives rise to a mixture of compounds **291** and **292**.

When α-phellandrene reacts with C_1-C_4 alcohols under the same conditions, compounds of type **293** are formed.[91] At the same time, alkoxylation of γ-terpinene **5** on zeolites of the 300 series affords ethers **294**.[92]



291 **292** **293** **294**

Some terpenoids undergo skeletal rearrangements during alkoxylation with C_1-C_4 alcohols. For example, dihydromyrcene **246** is converted into ether **295** with a terminal double bond, β-caryophyllene **21** yields tricyclic product **296**, and longifolene **9** gives products **297** and **298**.[92]



246 **295**

21 **296**

241 **297** **298**

IV. Conclusion

Analysis of the data considered in this review leads to interesting conclusions. The main of them is that many concepts and regularities of the chemistry of homogeneous reactions customary for organic chemists, such as homology, isomerism, vinylogy, *etc.*, cannot be transferred directly to the reactions of polyfunctional compounds occurring on the surface of heterogeneous catalysts (mostly aluminosilicates). In fact, even the closest homologues (acrolein and α-methylacrolein), vinylogues (formaldehyde and acrolein) and isomers (α-methylacrolein and crotonaldehyde) react in different ways in this case. The functional group in the reactant also does not play a crucial role: acrolein and α-methylacrolein react with camphene to give quite different products, whereas the products obtained from acrolein and methyl vinyl ketone are similar. The reaction route is determined not only by the structure of the reagent, but also by the structure of the substrate. For example, despite the fact that the bicyclic fragment in camphene and the benzene ring in styrene do not formally participate in the reaction with acrolein, which involves only the double bonds of these compounds, the reaction outcomes are totally dissimilar.

These speculations prompt the thought that the role of a heterogeneous catalyst does not always reduce to mere acid catalysis, although it is owing to the acid properties of the catalysts that some reactions can be conducted under milder conditions and their selectivities and the yields of products can be increased. However, the main role of a heterogeneous catalyst is to ensure a certain orientation of the molecule with simultaneous decrease in the energy barriers to many transformations, and this often sets the process on an unusual pathway.

The lack of understanding of the regularities of adsorption of even simple organic substrates on the surface of a catalyst hampers the prediction of the behaviour of complex polyfunctional compounds, such as terpenoids, under these conditions. The currently available experimental data permit only some empirical conclusions to be drawn. However, accumulation of knowledge in this interesting field of organic chemistry will certainly make it possible to generalise and classify the information and, hence, to predict with confidence the reactivities of various substrates. Finally, it should also be mentioned that, although the research in the field of reactions of terpenoids on heterogeneous catalysts is still being carried out by the 'trial and error' method, important and interesting results have already been obtained, owing to the polyfunctionality and conformational flexibility of the substrates under consideration and also owing to abnormal orientations, compared to those in homogeneous reactions, of reacting molecules on the surface of catalysts.

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