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HETEROGENEOUS CATALYTIC TRANSFORMATIONS OF NATURAL CAMPHENE

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Reactions of the natural terpene camphene with various reagents on zeolitic catalysts are reviewed.

Key words: camphene, zeolites, alkylation, acylation, nitration, reaction mechanisms.

The natural terpene camphene (**1**) occurs in turpentine and essential oils and is a popular research material because of its industrial availability and the practical value of products derived from it. The camphene skeleton undergoes in acidic media numerous rearrangements that are well studied in homogeneous systems [1]. In this review, we examine transformations of camphene and its reactions with various reagents on aluminosilicate catalysts, which are being used more frequently for fine organic synthesis.

Typical reagents were aromatic hydrocarbons, aliphatic and fatty-aromatic alcohols, phenols, aldehydes and ketones, acetic anhydride and acetylchloride, and dinitrogen tetroxide. These transformations on zeolites are acid-catalyzed electrophilic addition reactions of the olefinic double bond.

We attempted to elucidate the nature of the initially formed carbocations and their further transformations as a function of reagent structure. We examined the electrophiles H^+, C^+-electrophiles (EC^+), and heterocations NO_2^+, and NO^+. Cations **2** corresponding to the attacking electrophile were first formed:

1 **2**

R = CH_3, CH_2EC, CH_2NO_2, CH_2NO

Then, the course of the reaction depends on the nature of the substituent on cationic center C^2 and the number and position of nucleophilic centers in the reagent.

REACTIONS OF CAMPHENE INITIATED BY PROTON ADDITION

It has been noted [1] that the hydrocamphene cation **2** (R = CH_3) in HSO_3F—SO_2FCl undergoes two equally probable rearraangements: a 3,2-*exo*-methyl shift and a sequence of Wagner—Meerwein 6,2-hydride and Wagner—Meerwein shifts (WM-6,2 ~H-WM). This racemizes the initially optically active olefin **1**. Both racemic and optically active products were obtained. Thus, the ratio between the processes with retention of optical activity and with racemization depends on the nature of the reagent.

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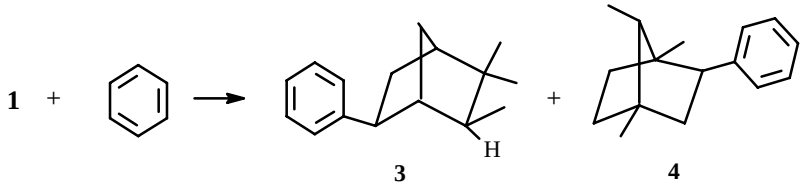
REACTIONS OF CARBONIUM IONS FORMED BY CAMPHENE PROTONATION WITH NUCLEOPHILES CONTAINING ONE OR MORE IDENTICAL CENTERS

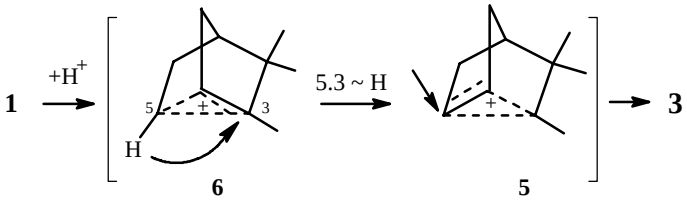
We will now discuss reactions of **1** with aromatic compounds on β-zeolite. We start with alkylation of aromatic hydrocarbons by **1**. Alkylation of aromatic compounds by various reagents on zeolites is one of the most studied and widely applied reactions. The reagents are usually simple alkenes, alcohols, and alkylhalides. The reactions are performed in the gas phase at high temperatures (150-400°C). Alkylation of aromatic hydrocarbons by terpenes on aluminosilicate catalysts is at present practically unstudied. Only the reaction of norbornadiene with aromatic hydrocarbons on H^+-zeolite to produce 3-*exo*-arylnortricyclenes and 5-*exo*-arylnorborn-2-enes has been reported [2].

It was found [3, 4] that racemic 2,2,3-*exo*-trimethyl-5-*exo*-phenylbicyclo[2.2.1]heptane (**3**) and 1,4,7-trimethyl-2-*exo*-phenylbicyclo[2.2.1]heptane (**4**) are formed in a 5:1 ratio (77% yield of the mixture) upon adding optically active **1** ($[\alpha]_{580}^{20}$ +12.5°, *c* 11.6, $CHCl_3$) to the reaction with benzene at room temperature (Scheme 1).



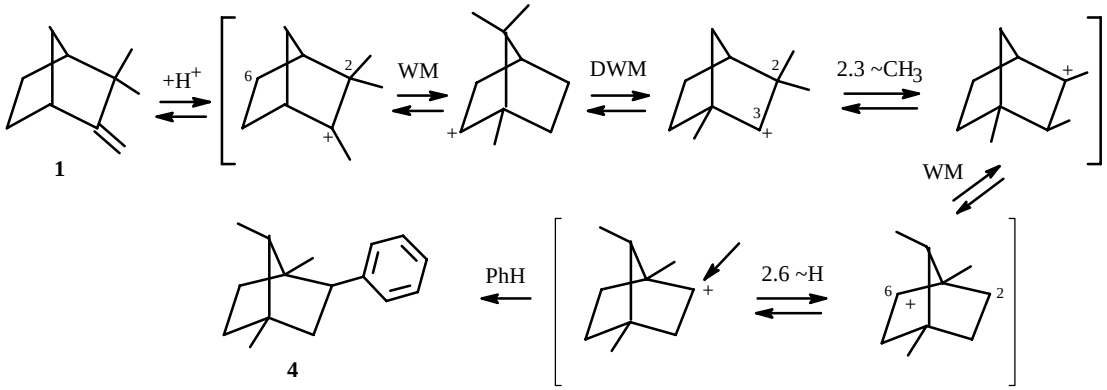
Scheme 1.

Let us note that the formation of the predominant reaction product **3** includes low-temperature alkylation and highly regioselective attack on carbocation **5** via a 5,3-shift of the H in cation **6** (Scheme 2). The conversion of the tertiary ion **6** into the secondary ion **5** may be due to a lowering of the energy difference between the isomeric secondary and tertiary ions through the nonclassical structure of **5**. Finally, the reaction is highly stereoselective, which can also be explained by the σ-delocalized structure of **6**.



Scheme 2.

The side product **4** has an unusual structure. However, a detailed study of the rearrangement of **6** by direct observation (NMR) [5] did not detect an isomer with 1,4,7-methyls. Scheme 3 presents a formation route to **4** that includes Wagner—Meerwein rearrangement (WM), double Wagner—Meerwein rearrangement (DWM), 2,3-*exo*-methyl shift, WM, and a 2,6-shift of H.

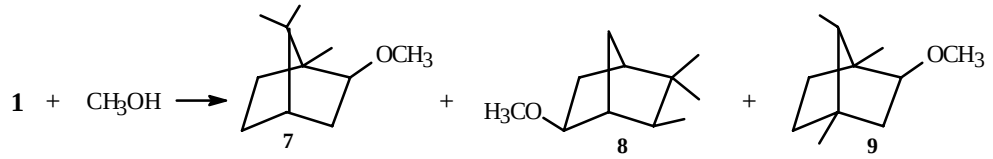


Scheme 3.

Obviously such a multi-step scheme argues in favor of the formation and relatively long life of carbocations on zeolites.

The appearance of optically inactive compounds **3** and **4** indicates that starting olefin **1** racemizes. Obviously racemization on zeolite occurs more rapidly than alkylation. It was observed [4] that only racemization occurs in a **1**—C_6H_6—AcOH mixture. Alkylation products are not formed.

Methanol also reacts with **1** under mild conditions to form 1,7,7-trimethyl-2-*exo*-methoxybicyclo[2.2.1]heptane (**7**) (24% yield), 2,2,3-*exo*-trimethyl-5-methoxybicyclo[2.2.1]heptane (**8**) (10%), and 1,4,7-*anti*-trimethyl-2-*exo*-methoxybicyclo [2.2.1]heptane (9) in a 70:17:13 ratio (Scheme 4) [6].

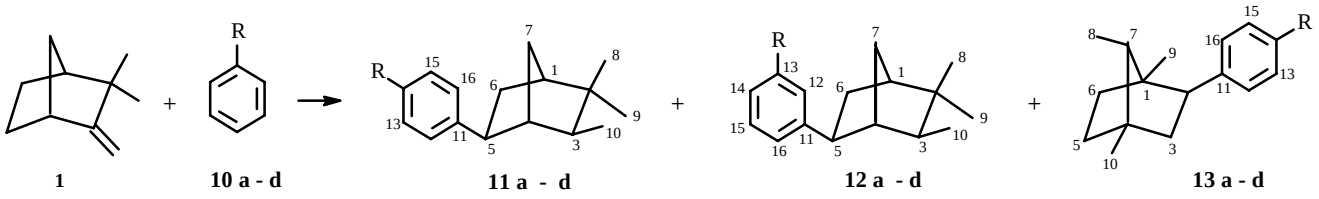


7 **8** **9**

Scheme 4.

REACTIONS OF CARBOCATIONS FORMED BY CAMPHENE PROTONATION WITH MULTICENTER NUCLEOPHILES

Reactions of hydrocamphene cation with aromatic hydrocarbons. Monoalkylated benzenes **10a-d** react with **1** on β-zeolite at room temperature to form racemic **11-13a-d** (Scheme 5) [4]. Use of zeolite catalysts to alkylate of monosubstituted benzenes leads to a predominance in the reaction mixture of the *p*-isomers. This indicates that zeolites are *p*-directing. However, ethylation of monoalkylbenzenes by ethylene on wide-pore β-zeolite is known to exert an *o*-directing effect [7], which was explained by kinetic control of the direction of substitution into the aromatic ring because of the relatively small size of the reactants and intermediates.



1 **10 a - d** **11 a - d** **12 a - d** **13 a - d**

R = CH_3 (**a**), CH_2-CH_3 (**b**), CH_2-CH_2-CH_3 (**c**), $C(CH_3)_3$ (**d**)

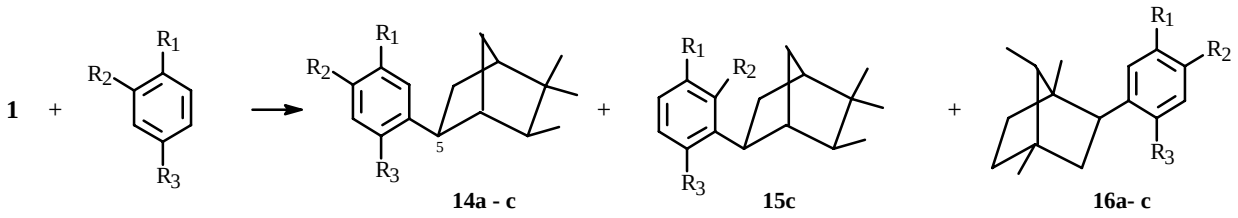
Scheme 5.

An analysis of the resulting [4] reaction mixtures shows that the overall yield of reaction products decreases from 60% for R = Me to 20% for R = *t*-Bu as the bulk of the alkyl substituent increases in monoalkylbenzenes. The main products in all mixtures are *p*-isomers **11a-d**. The relative content of *m*-isomers **12a-d** increases with increasing bulk of the alkyl substituent. Separate experiments determined that the *p*- and *m*-isomers do not interconvert. Minor amounts of compounds of type **13** appear in all instances.

Competing reactions were carried out on zeolite catalyst using benzene and toluene to determine the relative reaction rates of **1** with benzene and monoalkylbenzenes [4]. It was found that the alkylation rates of these compounds at 6, 20, and 80°C are practically identical, i.e., the nucleophilicity of the substrate has little effect on the reaction rate. These results were compared with those given in a review [8] where it was noted that steric and probability factors do not favor alkylation of benzene homologs if the alklating agent does not develop positive charge. Therefore, benzene can exhibit even greater activity than its homologs. For the heterogeneous reaction, it can be hypothesized that the similarity of the reaction rates of **1** with benzene and toluene is due to the fact that the attacking species is the relatively inactive σ-delocalized nonclassical ion **5**. Attempts to react **1** and monosubstituted benzenes containing substituents other than alkyls revealed that the reaction does not

occur even at temperatures up to 100°C. Aromatic compounds containing electron-donor (phenol, anisole) and electron-acceptor groups (nitrobenzene, benzaldehyde, chlorobenzene, fluorobenzene) do not react.

Either this factor or peculiarities of the adsorption of the reactants on the catalyst make isomeric xylenes less reactive toward **1** than benzene (Scheme 6).



R_1 = CH_3 (**a**, **c**), H (**b**); R_2 = H (**a**), CH_3 (**b**), CH_3 (**c**); R_3 = CH_3 (**a**, **b**), H (**c**)

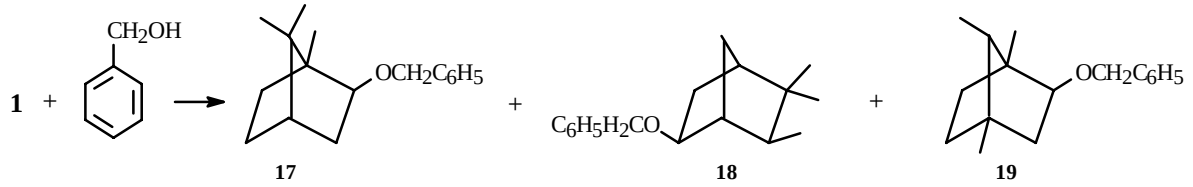
Scheme 6.

The overall product yield increases on going from *p*-xylene to *m*- and *o*-xylene; 10, 18, and 41%, respectively. Compounds of type **14** predominate in all reaction mixtures. Products with 1,4,7-methyls (**16a-c**) are also present. The absence of the isomer corresponding to substitution at C-5 of the *m*-xylene ring is interesting. At first glance, this is the most sterically available site. This might be explained by the unfavorable electronic effect of both methyls (the *m*-position of attack relative to both methyls). However, a comparison of the reactivity of *m*- and *o*-xylene shows that the former, which has a more favorable electronic subsituent effect (*o*- and *p*-methyls relative to the site of attack), is less reactive toward formation of compounds of type **14** than the latter, which has methyls in *p*- and *m*-positions. Obviously in this instance also peculiarities of the adsorption of the reagents on zeolite are the determining factor.

The increase in the number of methyls on going from xylenes to mesitylene causes the latter to be unreactive toward **1**. Naphthalene and biphenyl also do not react with **1** although successful alkylation by lower olefins on zeolites has been reported many times [9]. Pyridine does not react with **1** on zeolite even with heating to 115°C.

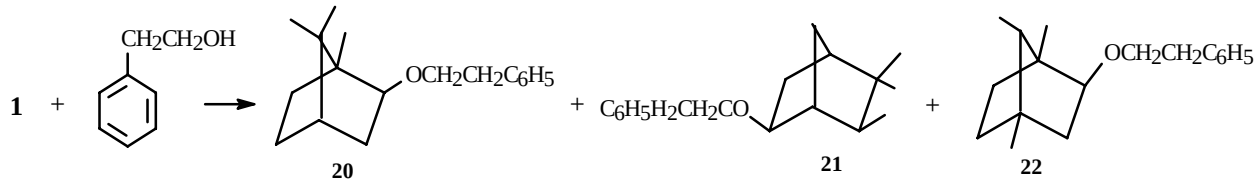
RATIO OF O- AND C-ALKYLATION OF HYDROCAMPHENE CATION BY ALIPHATIC AND FATTY-AROMATIC ALCOHOLS

The reaction of **1** on β-zeolite with aromatic compounds changes direction if the side chain contains a hydroxyl. Reacting benzyl alcohol and **1** on zeolite results in O-alkylation rather than C-alkylation to produce the racemic ethers 1,7,7-trimethyl-2-*exo*-benzyloxybicyclo[2.2.1]heptane (**17**), 2,2,3-*exo*-trimethyl-5-*exo*-benzyloxybicyclo[2.2.1]heptane (**18**), and 1,4,7-*anti*-trimethyl-2-*exo*-benzyloxybicyclo[2.2.1]heptane (**19**) in the ratio 8:1:1, respectively (70% yield of the mixture) (Scheme 7) [10].



Scheme 7.

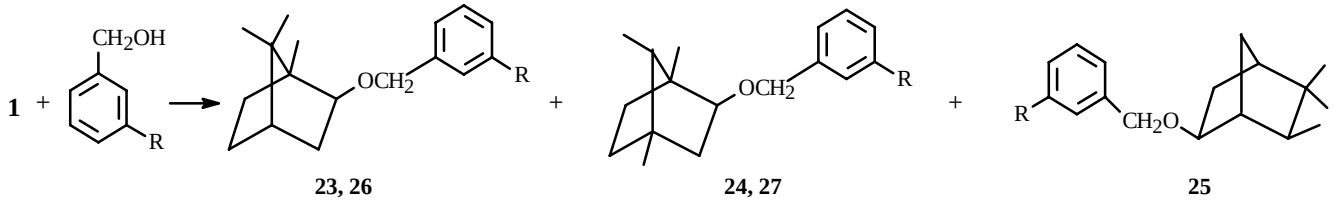
Under these same conditions, β-phenethanol reacts with **1** to form racemic 1,7,7-trimethyl-2-*exo*-phenethoxybicyclo [2.2.1]heptane (**20**), 2,2,3-*exo*-trimethyl-5-*exo*-phenethoxybicyclo[2.2.1]heptane (**21**), and 1,4,7-*anti*-trimethyl-2-*exo*-phenethoxybicyclo[2.2.1]heptane (**22**) in a 5:3:1 ratio, respectively (53% yield of the mixture) (Scheme 8).



Scheme 8.

In order to explain the effect of the aromatic substituents on the course of the reaction of alcohols and **1**, reactions of substituted benzyl alcohols containing both electron-acceptor (*p*-nitrobenzyl alcohol) and electron-donor (*p*-methoxybenzyl alcohol) substituents were studied. It was found that introducing either electron-donor or -acceptor substituents into the aromatic ring does not cause the corresponding alcohols to react with **1**. This is evidently due to the equalizing of substituent electronic effects if the reaction is carried out under the selected conditions.

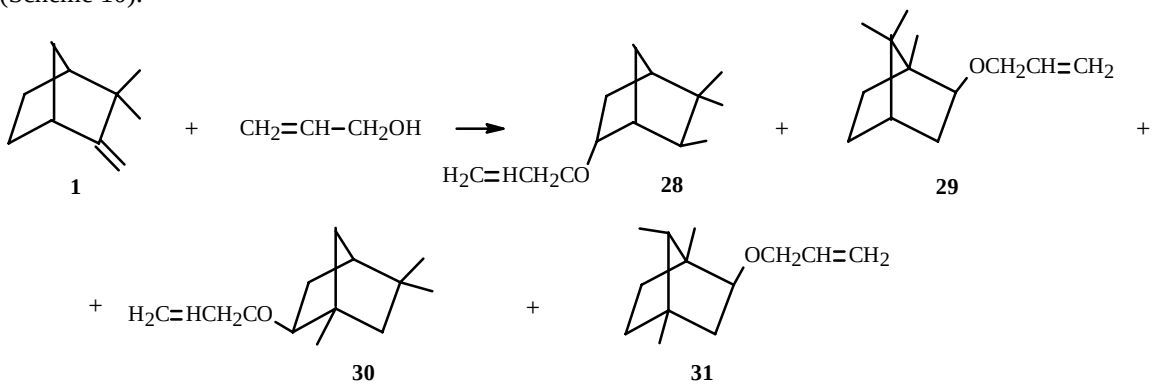
However, alkoxylation of **1** accelerates if a methyl or Br is introduced into the *m*-position of the benzyl. The electronic effects of these in this position are known to be small. Reaction of **1** with *m*-methylbenzyl alcohol produces the three racemic ethers 1,7,7-trimethyl-2-*exo*-(*m*-methylbenzyloxy)bicyclo[2.2.1]heptane (**23**) (18% yield), 1,4,7-*anti*-trimethyl-2-*exo*-(*m*-methylbenzyloxy)bicyclo[2.2.1]heptane (**24**) (6%), and 2,2,3-*exo*-trimethyl-5-*exo*-(*m*-methylbenzyloxy)bicyclo[2.2.1]heptane (**25**) (2%). Reaction of *m*-bromobenzyl alcohol with **1** forms 1,7,7-trimethyl-2-*exo*-(*m*-bromobenzyloxy)bicyclo[2.2.1]heptane (**26**) (55% yield) and 1,4,7-*anti*-trimethyl-2-*exo*-(*m*-bromobenzyloxy)bicyclo[2.2.1]heptane (**27**) (2%) (Scheme 9).



23, 24, 25: R = CH_3; **26, 27:** R = Br

Scheme 9.

Not only fatty-aromatic alcohols react with **1**. Reaction of allyl alcohol with **1** under mild conditions produces a mixture of 2,2,3-*exo*-trimethyl-5-*exo*-allyloxybicyclo[2.2.1]heptane (**28**) and 1,7,7-trimethyl-2-*exo*-allyloxybicyclo[2.2.1]heptane (**29**) in 29 and 65% yields, respectively. In addition to the main products, a small amount (~6%) of a 1:0.6 mixture of 2,2,4-trimethyl-5-*exo*-allyloxybicyclo[2.2.1]heptane (**30**) and 1,4,7-*anti*-trimethyl-2-*exo*-allyloxybicyclo[2.2.1]heptane (**31**) was obtained (Scheme 10).



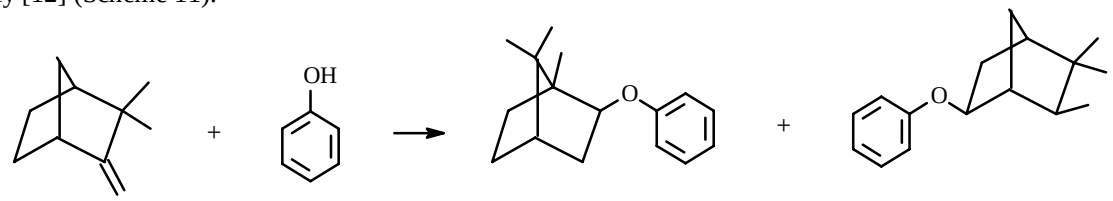
Scheme 10.

Compounds of type **30** were not previously obtained from reactions of fatty-aromatic alcohols [6].

RATIO OF O- AND C-ALKYLATION OF HYDROCAMPHENE CATION BY PHENOLS

Phenol, which, like benzyl alcohol, contains an aromatic ring and hydroxyl, did not react with **1** under standard conditions (β-zeolite, 2-100°C, CH_2Cl_2 solvent). The low reactivity of phenol can be explained by its adsorption on the same Bronsted centers of zeolite that are responsible for the conversion of **1** into the hydrocamphene cation **2**, which is the attacking species in this reaction.

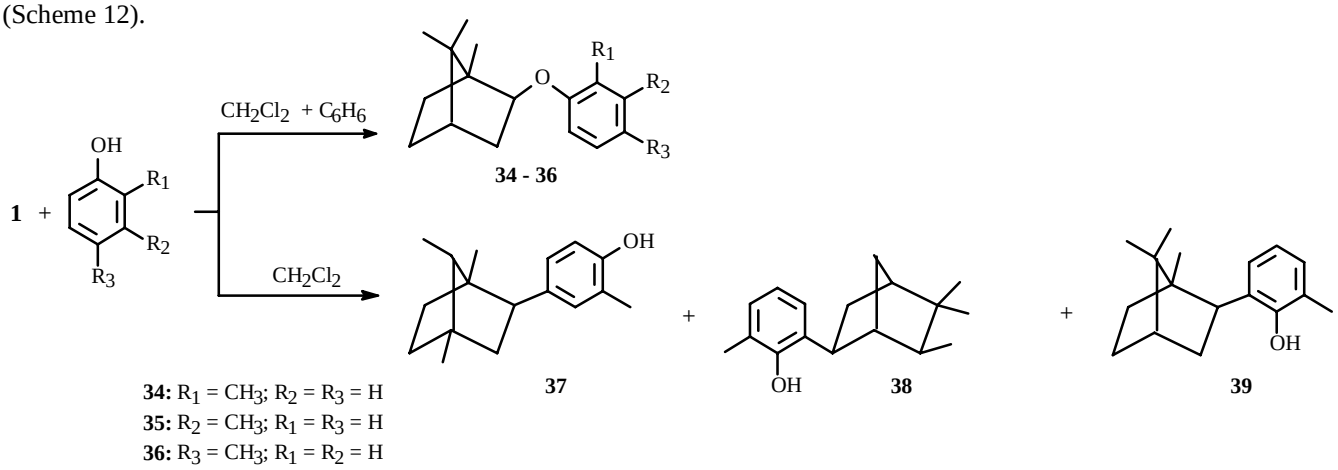
Phenol can be desorbed either by increasing the temperature [11] or by using solvents that can separate the adsorbed molecules from the centers that protonate the reagent [12]. In fact, using the solvent mixture CH_2Cl_2—C_6H_6 (1:1 by volume) instead of CH_2Cl_2 for the alkylation of phenol by the olefin **1** produces the terpenylphenyl ethers 1,7,7-trimethyl-2-*exo*-phenoxybicyclo[2.2.1]heptane (**32**) and 2,2,3-*exo*-trimethyl-5-*exo*-phenoxybicyclo[2.2.1]heptane (**33**) in 60 and 8% yield, respectively [12] (Scheme 11).



1 **32** **33**

Scheme 11.

Isomeric cresols in CH_2Cl_2—C_6H_6 also form the ethers 1,7,7-trimethyl-2-*exo*-(2-methylphenoxy)bicyclo[2.2.1]heptane (**34**), 1,7,7-trimethyl-2-*exo*-(3-methylphenoxy)bicyclo[2.2.1]heptane (**35**), and 1,7,7-trimethyl-2-*exo*-(4-methylphenoxy) bicyclo[2.2.1]heptane (**36**) in 29, 51, and 53% yield, respectively. Like unsubstituted phenol, *m*- and *p*-cresol do not react with camphene in CH_2Cl_2 whereas *o*-cresol forms the aromatic substitution products 1,4,7-*anti*-trimethyl-2-*exo*-(3-methyl-4-hydroxyphenyl)bicyclo[2.2.1]heptane (**37**), 2,2,3-*exo*-trimethyl-5-*exo*-(2-hydroxy-3-methylphenyl)bicyclo[2.2.1] heptane (**38**), and 1,7,7-trimethyl-2-*exo*-(2-hydroxy-3-methylphenyl)bicyclo[2.2.1]heptane (**39**) (33, 3, and 1.5% yield, respectively) [12] (Scheme 12).

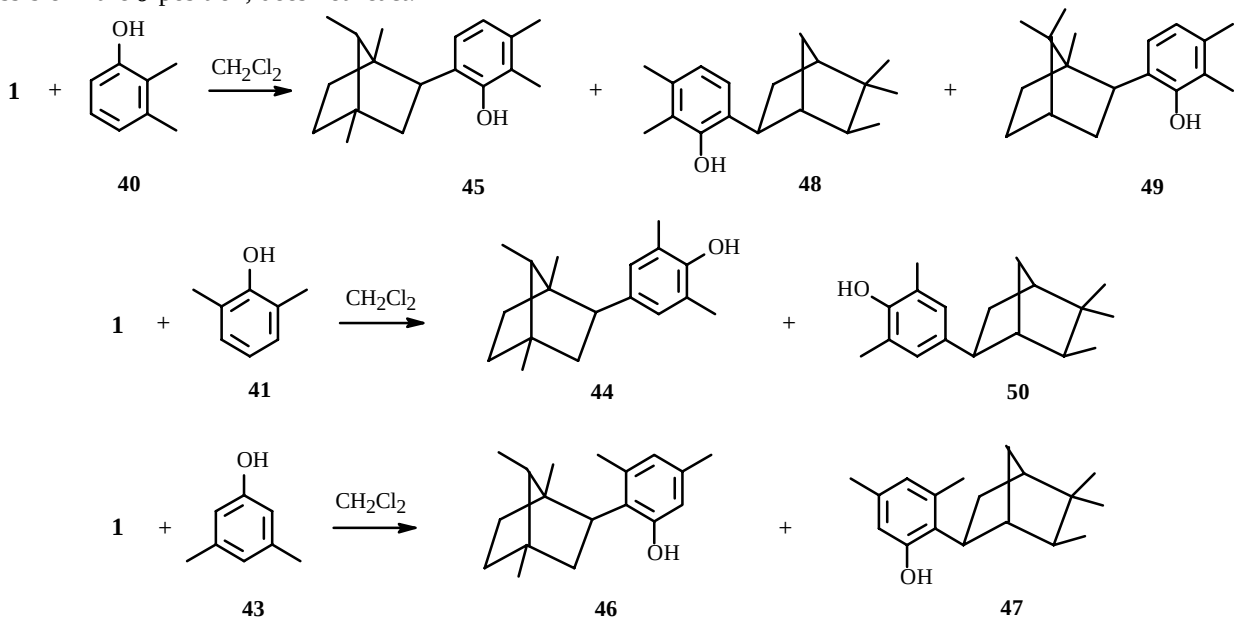


Scheme 12.

The main product in the last instance is **37** with the unusual 1,4,7-position of methyls in the alicyclic skeleton. Recall that products with this position were the minor ones for C-alkylation of aromatic hydrocarbons or O-alkylation of fatty-aromatic alcohols by **1**.

Increasing the number of methyls on going to the disubstituted phenols led to the following results. In contrast with phenol and cresols, disubstituted phenols 2,3-dimethylphenol (**40**), 2,6-dimethylphenol (**41**), 2,4-dimethylphenol (**42**), and 3,5-dimethylphenol (**43**) do not react with **1** in CH_2Cl_2—C_6H_6 and do not form ethers even for **43**, which has no *o*-substituents and lacks the corresponding steric hindrances to O-alkylation. All these substrates, except for **42**, are C-alkylated on the aromatic ring in CH_2Cl_2. The main product from phenol **41** results from *p*-substitution of the aromatic ring by the terpene with 1,4,7-

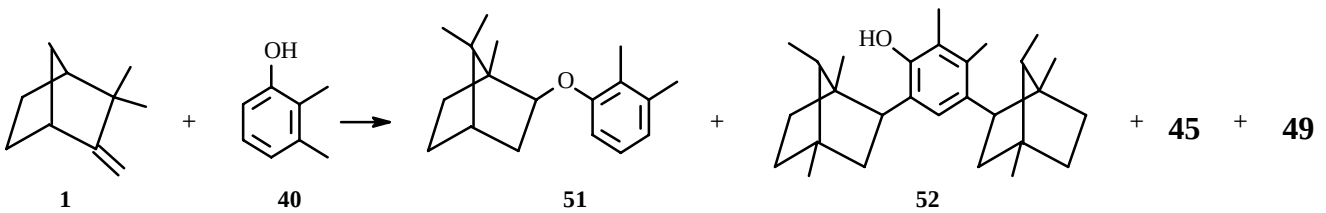
methyls, 1,4,7-*anti*-trimethyl-2-*exo*-(4-hydroxy-3,5-dimethylphenyl)bicyclo[2.2.1]heptane (**44**) in 52% yield. Compounds **40** and **43** undergo attack at the *o*-position to give also main products with 1,4,7-methyls in the alicyclic skeleton, 1,4,7-*anti*-trimethyl-2-*exo*-(2-hydroxy-3,4-dimethylphenyl)bicyclo[2.2.1]heptane (**45**) (26% yield) and 1,4,7-*anti*-trimethyl-2-*exo*-(2-hydroxy-4,6-dimethylphenyl)bicyclo[2.2.1]heptane (**46**) (45%). In addition, **42** forms 2,2,3-*exo*-trimethyl-5-*exo*-(2-hydroxy-4,6-dimethylphenyl)bicyclo[2.2.1]heptane (**47**) (31% yield) (Scheme 13). Phenol **42**, which is blocked in the *p*-position but accessible in the *o*-position, does not react.



Scheme 13.

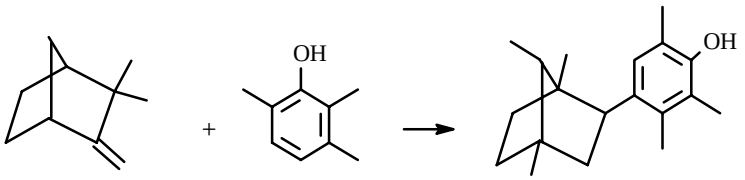
Compound **40** reacts with **1** to give **45** and products of *o*-substitution by isocamphyl, 2,2,3-*exo*-trimethyl-5-*exo*-(2-hydroxy-3,4-dimethylphenyl)bicyclo[2.2.1]heptane (**48**), and isobornyl, 1,7,7-trimethyl-2-*exo*-(2-hydroxy-3,4-dimethylphenyl) bicyclo[2.2.1]heptane (**49**), in approximately equal amounts (10% yield of each).

The solvent effect on the reaction path was examined in more detail using the reaction of **41** and **1** [12]. Reactions were carried out in CH_2Cl_2 ($\varepsilon = 8.9$), CH_2Cl_2—C_6H_6, benzene ($\varepsilon = 2.28$), cyclohexane ($\varepsilon = 2.02$), and *n*-hexane ($\varepsilon = 1.89$). It was found that the dielectric permeability of the solvent has no substantial effect on the path. The reaction occurs identically in CH_2Cl_2, cyclohexane, and *n*-hexane [in the last two instances the products include **44** (24 and 39% yields, respectively) and 2,2,3-*exo*-trimethyl-5-*exo*-(4-hydroxy-3,5-dimethylphenyl)bicyclo[2.2.1]heptane (**50**) (3.5 and 3% yields, respectively)]. However, the reaction does not occur in benzene. It should be noted that the skeleton of the solvent has no effect on the direction of the reaction. Thus, the results are practically identical in cyclohexane and *n*-hexane. Varying the solvents, at least for dimethylphenols, does not induce O-alkylation. However, the principal direction of the reaction of **40** with a five-fold excess of **1** is formation of the terpenylphenylether 1,7,7-trimethyl-2-*exo*-(2,3-dimethylphenoxy)bicyclo[2.2.1]heptane (**51**) (31% yield, Scheme 14). The first product identified and isolated in this reaction results from substitution of the aromatic ring by two terpenes, 2,3-dimethyl-4,6-di(1,4,7-*anti*-trimethylbicyclo[2.2.1]heptyl)phenol (**52**) in 5% yield. Besides these compounds, products of monosubstitution of the aromatic ring by terpene, **45** and **49**, are isolated in yields of 11 and 4%, respectively.



Scheme 14.

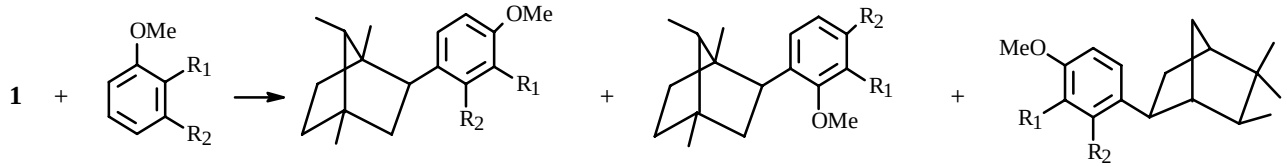
Reaction of 2,3,6-trimethylphenol (**53**) with **1** produces 1,4,7-*anti*-trimethyl-2-*exo*-(2,3,5-trimethyl-4-hydroxyphenyl) bicyclo[2.2.1]heptane (**54**) in 40% yield [12] (Scheme 15).



1 **53** **54**

Scheme 15.

Mesitol, 2,3,5-trimethylphenol, durenol, and pentamethylphenol do not react with **1** if CH_2Cl_2 or CH_2Cl_2—C_6H_6 systems are used as solvents. Anisole (**55**), 2-methylanisole (**56**), and 3-methylanisole (**57**) react with **1** to give principal products that are *p*-substituted with respect to the methoxy: 1,4,7-*anti*-trimethyl-2-*exo*-(4-methoxyphenyl)bicyclo[2.2.1]heptane (**58**) (17% yield), 1,4,7-*anti*-trimethyl-2-*exo*-(2-methyl-4-methoxyphenyl)bicyclo[2.2.1]heptane (**59**) (30%), and 1,4,7-*anti*-trimethyl-2-*exo*-(2-methyl-4-methoxyphenyl)bicyclo[22.1]heptane (**60**) (19%). The terpene skeleton has primarily 1,4,7-methyls for both the main and side products, 1,4,7-*anti*-trimethyl-2-*exo*-(2-methoxyphenyl)bicyclo[2.2.1]heptane (**61**) (3% yield) and 1,4,7-*anti*-trimethyl-2-*exo*-(2-methoxy-4-methylphenyl)bicyclo[2.2.1]heptane (**62**) (6%), that are formed by reaction of **1** with anisoles **55** and **57**, respectively. The terpene skeleton has a different structure for the minor products, 2,2,3-*exo*-trimethyl-5-*exo*-(4-methoxyphenyl)bicyclo[2.2.1]heptane (**60**) (8% yield) and 2,2,3-*exo*-trimethyl-5-*exo*-(2-methyl-4-methoxyphenyl) bicyclo[2.2.1]heptane (**61**) (2%), isolated from these same reaction mixtures (Scheme 16). 4-Methylanisole under these conditions does not react.



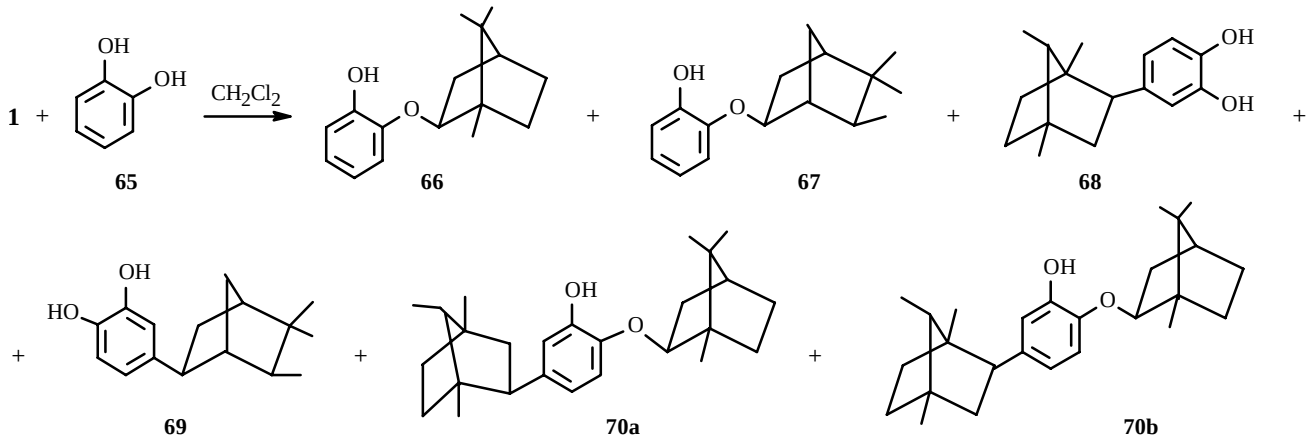
55 - 57 **58 - 60** **61, 62** **63, 64**

55, 58, 61, 63: $R_1 = R_2 = H$; **56, 59:** $R_1 = CH_3$, $R_2 = H$; **57, 60, 62, 64:** $R_1 = H$, $R_2 = CH_3$

Scheme 16.

Thus, the literature review showed that two types of processes are possible for alkylation of phenol, anisole, and their substituted derivatives by **1** on wide-pore β-zeolite depending on the substrate structure and solvent. These are O-alkylation with formation primarily of terpene ethers of isobornyl structure in the alicyclic moiety and C-alkylation with formation primarily of the corresponding terpenylphenols and anisoles of unusual structure in the terpene fragment, 1,4,7-methyls in the alicyclic moiety. In this instance, alkylation of the aromatic species is highly *p*-selective. Special attention should be paid to the fact that alkylation of alkyl-substituted benzenes and fatty-aromatic alcohols by **1** forms products with 1,4,7-methyls in only small amounts whereas they are the main products of alkylation of phenols.

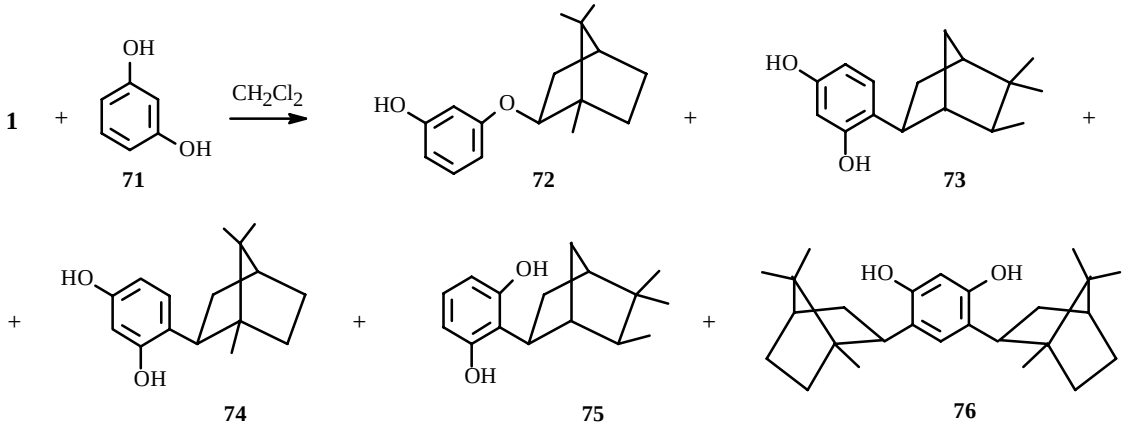
When the assortment of aromatic reagents was expanded [13] and **1** was reacted with various dihydroxybenzenes, important differences were observed in their reactivity compared with that of aromatic substrates. Thus, reaction of **1** and pyrocatechol (**65**) in CH_2Cl_2 occurs via O-alkylation to form 1,7,7-trimethyl-2-*exo*-(2-hydroxyphenoxy)bicyclo[2.2.1]heptane (**66**) and 2,2,3-*exo*-trimethyl-5-*exo*-(2-hydroxyphenoxy)bicyclo[2.2.1]heptane (**67**) in 30 and 4.5% yields, respectively, and via C-alkylation to form 1,4,7-*anti*-trimethyl-2-*exo*-(3,4-dihydroxyphenyl)bicyclo[2.2.1]heptane (**68**) and 2,2,3-*exo*-trimethyl-5-*exo*-(3,4-dihydroxyphenyl)bicyclo[2,2,1]heptane (**69**) in 9 and 11% yields, respectively. In addition, C- and O-alkylation of phenol to give 1,4,7-*anti*-trimethyl-2-*exo*-(3-hydroxy-4-isobornyloxyphenyl)bicyclo[2.2.1]heptane (**70**) in 5.5% yield was observed for the first time (Scheme 17)



Scheme 17.

According to ^{1}H and ^{13}C NMR spectra, compound **70** is formed as a mixture of diastereomers **70a** and **70b** in approximately equal amounts.

Reaction of **1** with resorcinol (**71**) in CH_2Cl_2, like in the previous instance, gave the O-alkylation product 1,7,7-trimethyl-2-*exo*-(3-hydroxyphenoxy)bicyclo[2.2.1]heptane (**72**) in 21% yield and the C-alkylation products 2,2,3-*exo*-trimethyl-5-*exo*-(2,4-dihydroxyphenyl)bicyclo[2.2.1]heptane (**73**), 1,7,7-trimethyl-2-*exo*-(2,4-dihydroxyphenyl)bicyclo[2.2.1]heptane (**74**), and 2,2,3-*exo*-trimethyl-5-*exo*-(2,6-dihydroxyphenyl)bicyclo[2.2.1]heptane (**75**) in 18, 14, and 2.5% yields, respectively, in addition to the product of dialkylation of compound **71**, 2,4-diisobornylresorcinol (**76**), in 2% yield (Scheme 18).



Scheme 18.

It should be noted especially that C-alkylation of an aromatic substrate by **1** earlier gave products with 1,4,7-methyls in the alicyclic skeleton. Such products were minor for alkylation of aromatic hydrocarbons. However, they are the principal ones for phenols. The expected terpenylphenols with 1,4,7-methyls in the alicyclic moiety do not result from the reaction of **71** [13].

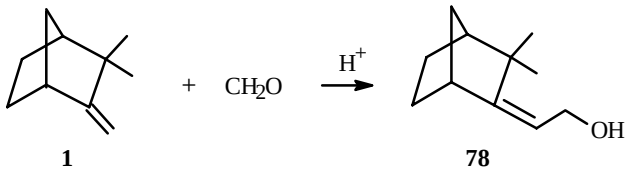
An attempt to react hydroquinone (**77**) with **1** gave an exceedingly complicated product mixture without predominance of any one compound. Phenols **65**, **71**, and **77** did not react with **1** in CH_2Cl_2—C_6H_6 [10].

Thus, reaction of **1** with dihydroxybenzenes in CH_2Cl_2 on wide-pore β-zeolite gives products of both O- and C-alkylation of phenol. In addition to these compounds, products of dialkylation of phenol and the O atoms is possible.

REACTIONS OF CAMPHENE INITIATED BY C-ELECTROPHILE ADDITION

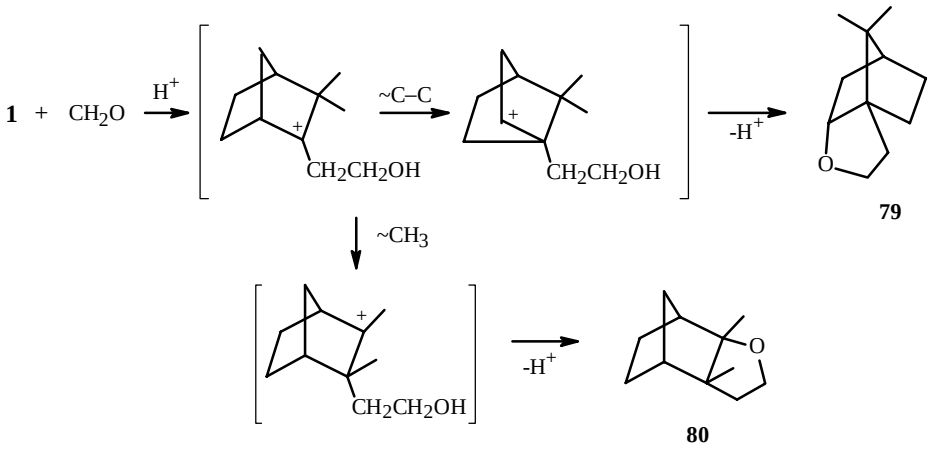
Reactions of camphene with aldehydes and ketones. These reactions are initiated by C-electrophiles formed from carbonyls. Let us start with the reaction of **1** and formaldehyde [14]. Condensation of these compounds in the presence of acid

catalysts is well studied. The products are 8-hydroxymethylcamphene (**78**) or its ethers (Scheme 19).



Scheme 19.

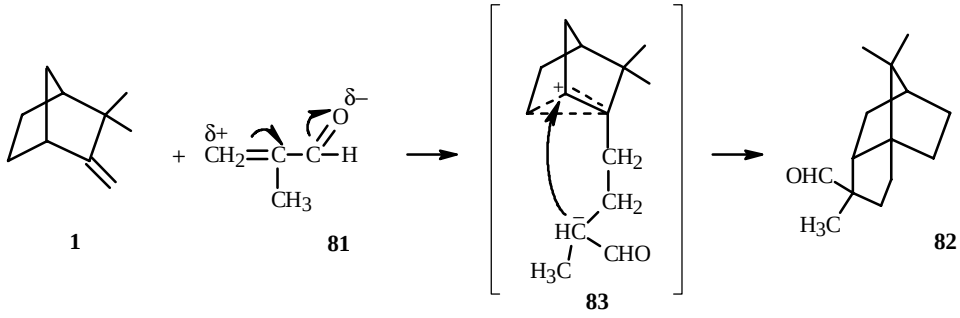
Performing this reaction on β-zeolite changes the principal direction to formation of skeletal rearrangement products, tricyclic ethers 10,10-dimethyl-4-oxatricyclo[5.2.1.0^{1,5}]decane (**79**) and 2,6-dimethyl-3-oxatricyclo-[5.2.1.0^{2,6}]decane (**80**) (Scheme 20) [14].



Scheme 20.

The first step involves attack of protonated formaldehyde on the olefinic double bond of **1**. Then, the reaction follows two paths. These are 1) WM rearrangement and stabilization of the positive charge by formation of a bond to the O atom to give **79** and 2) a 1,2-shift of the *exo*-methyl and stabilization of the resulting cation to give **80**. Starting **1** is optically active. The products **79** and **80** are racemic. It was found [14] that **1** racemizes on β-zeolite at room temperature whereas **79** and **80** are formed at 100°C.

Now let us exam reactions of **1** and α,β-unsaturated carbonyls, which occur owing to polarization of the olefinic double bond. Reaction of **1** and α-methylacrolein (**81**) on β-zeolite produces a compound with a tricyclic skeleton, 4-formyl-4,4,10-trimethyltricyclo[5.2.1.0^{1,5}]decane (**82**) in 52% yield (Scheme 21) [15].

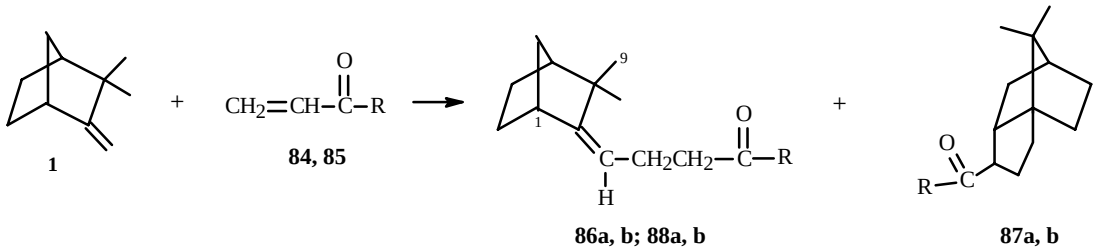


Scheme 21.

The reaction begins obviously with initial attack by the polarized β-olefin C of the aldehyde to form **83**. The carbonium ion is stabilized intramolecularly via interaction with the carbanion. This forms the new carbocycle with the aldehyde in the side chain. If the reactions of **1** with formaldehyde and **81** on zeolite are compared, [3+2]-cyclization is observed in both

instances. In the first, this is heterocyclization to form the cyclic ether; in the second, carbocyclization to form the aldehyde. The electrophile in the reaction with formaldehyde is the carbonyl C. The nucleophile is the O atom. The β-olefinic C acts as the electrophile in the reaction with **81**; the carbanion, as the nucleophile.

Let us now examine the reaction of **1** and acrolein (**84**) and methylvinylketone (**85**) on β-zeolite [16]. The product mixture consists mainly of (**86a** + **88a**) and (**86b** + **88b**), respectively. These are pairs of geometric isomers that can be considered formally as substitution products of the vinyl H. Products of carbocyclization **87a** and **b** are formed as minor products (Scheme 22).



84, 86 - 88a: R = H; **85, 86 - 88b:** R = CH_3

Scheme 22.

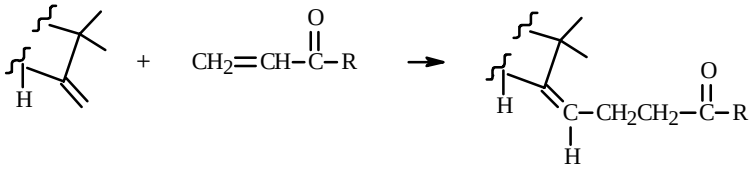
Reaction of **1** and **84** forms a mixture consisting of **86a** (57%) and **88a** (11%), which are assigned the 3-(8-camphenyl)propan-1-al structures, and 4-formyl-10,10-dimethyltricyclo[5.2.1.0^{1,5}]decane (**87a**) (18%). Reaction of **1** and **85** produces a mixture containing **86b** (59%) and **88b** (10%), which are characterized as the 4-(8-camphenyl)butan-2-ones and 4-acetyl-10,10-dimethyltricyclo[5.2.1.0^{1,5}]decane (**87b**) (31%).

According to Dreiding models and based on the chemical shifts of the signals for C-1 and C-9 in the ^{13}C NMR spectra of the pairs **86a**-**88a** and **86b**-**88b**, C-1 in **86a** and **b** experiences steric strain compared with that in **88a** and **b** whereas C-9 has slight steric strain in **88a** and **b**. Therefore, the C-10 substituent in **86a** and **b** is *cis* to C-1 whereas in **88a** and **b** it is *trans*.

It should be noted that these reactions in glacial acetic acid instead of on zeolite do not give the compounds mentioned above even with boiling. Acrylonitrile and crotonaldehyde did not react with **1** at 90°C. This indicates that, on one hand, the degree of polarization of the double bond plays an insignificant role; on the other, a β-CH_3 in α,β-unsaturated carbonyls creates steric hindrance to condensation with monoolefins on zeolites.

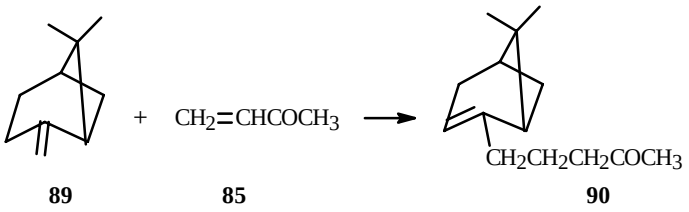
We now attempt to classify the observed substitution of vinyl H and discuss possible mechanisms. The resulting products are most similar to those of two well-known processes, ene synthesis and the Prins reaction. However, there are several differences in our instance. According to Snider and Gloman [17], the ene synthesis is considered to be the reaction of an alkene ("ene") containing an allylic H with a compound containing a double or triple bond ("enophile"). The result is the formation of a new bond and the migration of the ene accompanied by a 1,5-H shift.

The literature contains examples of the use of **84** and **85** as enophiles. For example, these react with methylcyclohexene in the presence of Lewis-acid catalysts to form standard adducts of ene synthesis [18]. In our instance, **1** acts as the ene (alkene) containing an allylic H; **84** or **85**, as the enophile. The reaction produces two σ-bonds, C–C and C–H, but the double bond does not migrate and the allylic H does not undergo a 1,5-shift (Scheme 23). Therefore, the observed transformation does not conform to the definition of ene synthesis.



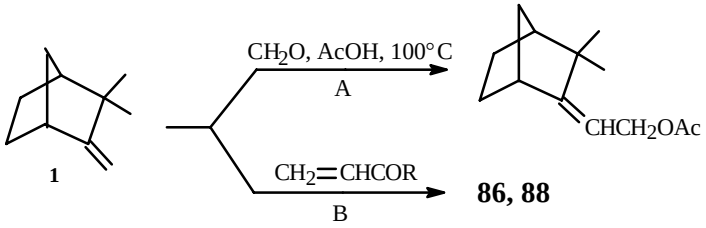
Scheme 23.

However, using β-zeolite as a catalyst for the reaction of β-pinene (**89**), which has a more mobile allylic H than **1**, and **85** produces the product of a typical ene synthesis, 2-(4-oxopentyl)-6,6-dimethylbicyclo[3.1.1]hept-2-ene (**90**) in 28% yield (Scheme 24).



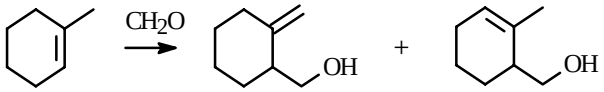
Scheme 24.

Let us compare the observed transformation of **1** with the Prins reaction (Scheme 25).



Scheme 25.

The Prins reaction (A) involves the reaction of a protonated aldehyde (practically always formaldehyde, $^{+}CH_2OH$) with a double bond to convert the carbonyl into an alcohol or the corresponding ether. Olefins and formaldehyde react thermally and without a catalyst to give products of ene synthesis (Scheme 26).

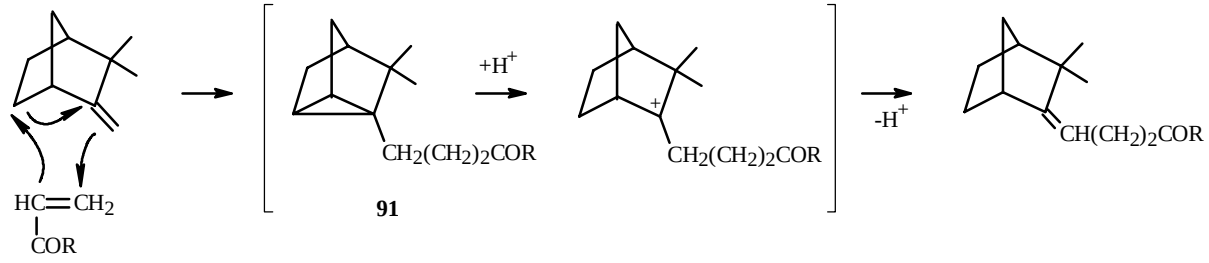


Scheme 26.

Reactions of carbonyls and olefins on zeolites (**B**) involve initial attack by the β-olefin C of the polarized double bond. The carbonyl is unchanged in the reaction product.

Thus, the observed process is not classified as a Prins reaction. Such a reaction is called "pseudoene" synthesis.

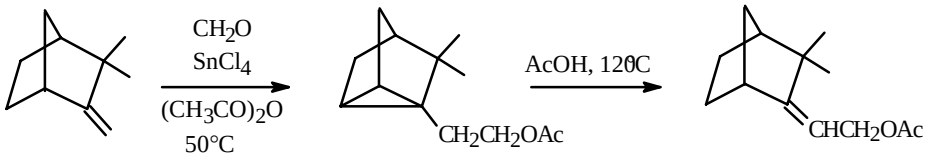
One of the possible mechanisms of pseudoene synthesis includes a sequence of transformations (Scheme 27) with the tricyclene intermediate **91**.



R = H; CH_3

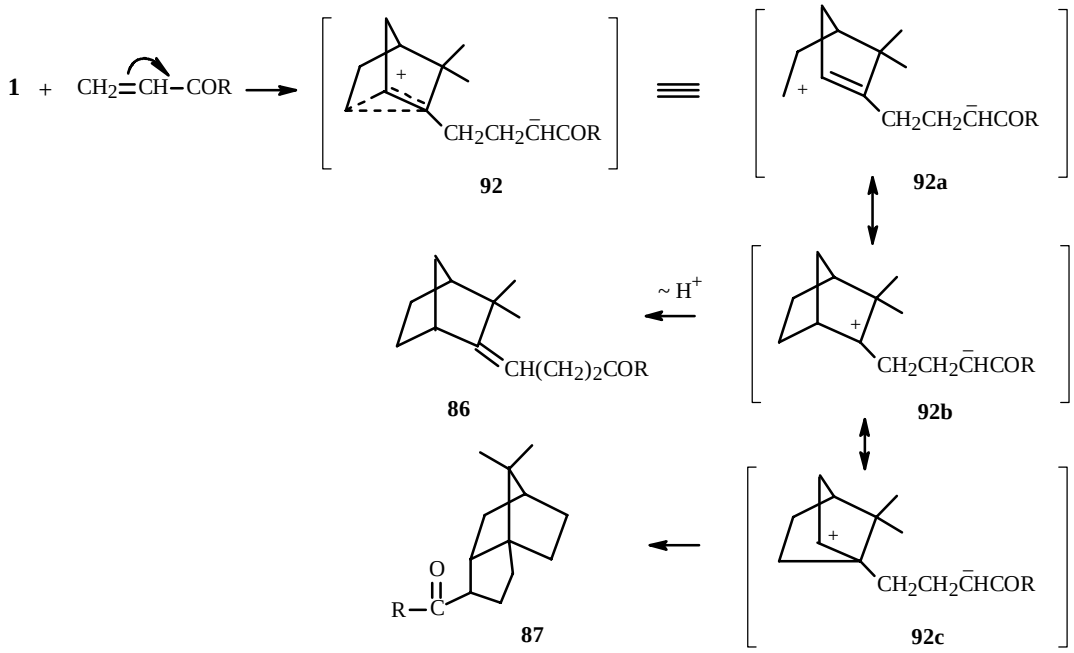
Scheme 27.

This type of reaction has been reported [19] (Scheme 28). However, the resulting tricyclic product is stable in the presence of Lewis acid at 50°C and transforms into the bicyclic compound only upon boiling in AcOH.



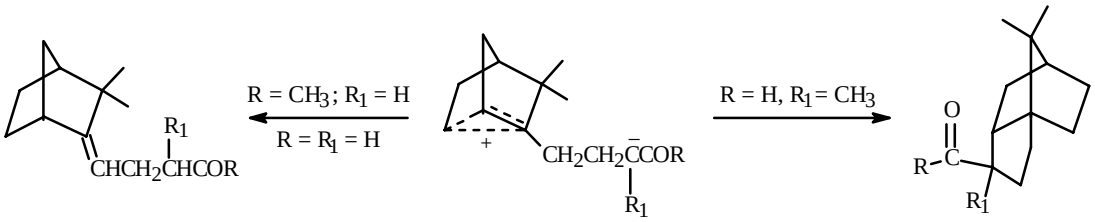
Scheme 28.

Therefore, if the transformation mechanism is considered to be that pictured in Scheme 27, then we should obtain tricyclic products under the conditions at which the studied reactions were conducted. This does not occur. Furthermore, the increase with time of the fraction of tricyclene (which was found in the starting olefin) indicates that the tricyclene under these conditions does not isomerize into **1**. In our opinion, a possible mechanism for reaction **B** is that given in Scheme 29.



Scheme 29.

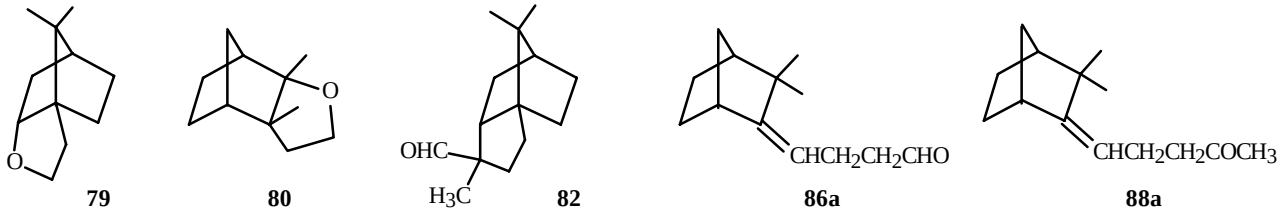
The intermediate nonclassical carbonium ion **92**, which can be represented by several resonance structures **92a-c**, either undergoes carbocyclization **92c→87** or forms a double bond **92b→86**. The ratio of these paths is determined by the nature of R_1, which apparently affects the geometric structure of the intermediate (Scheme 30).



Scheme 30.

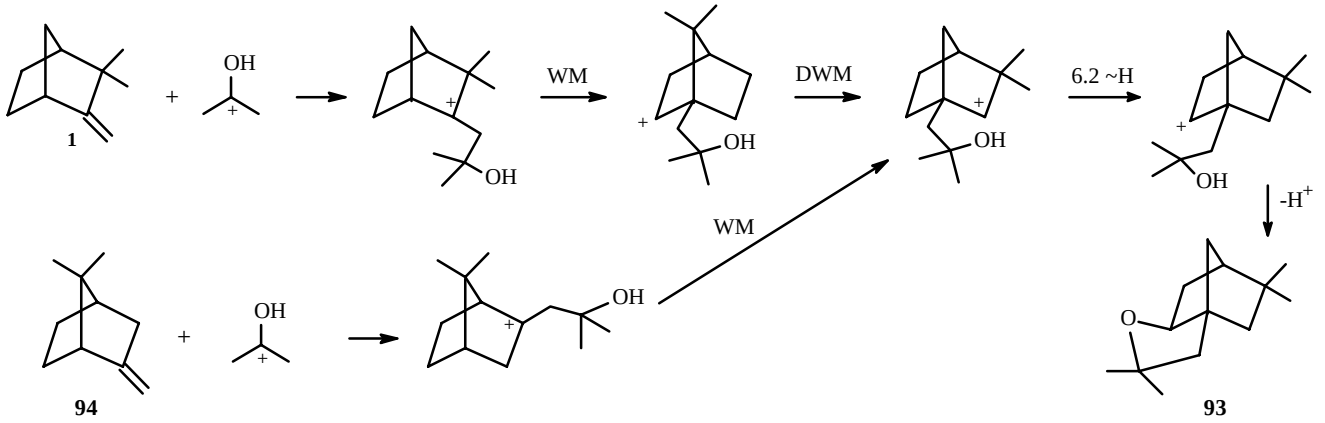
In concluding the discussion of the mechanism, we note that starting **1** was optically active. The resulting products were also optically active. This indicates that pseudoene synthesis and carbocyclization have faster rates compared with those of protonation and racemization of **1** on zeolite. Compounds **86b** and **87a** and **-b** that were isolated by Tatarova et al. [16] were not previously reported. Compound **86a** was first prepared by Borowiecki et al. [20] and then used as an intermediate in the synthesis of juvenile hormone analogs [21].

Thus, according to the literature, the reaction path of **1** on zeolite catalysts with various carbonyls depends substantially on their structures. Reaction of **1** with formaldehyde on wide-pore β-zeolite produced tricyclic ethers **79** and **80**; with **81**, tricyclic aldehyde **82**; with **84**, substitution products of the vinylic H in **1, 86a** and **88a**. Camphene (**1**) reacts analogously with methylvinylketone **85** to give **86b** and **88b**.



79 **80** **82** **86a** **88a**

We then showed that acetone on β-zeolite reacts differently than **85** with **1** to give the optically active heterocyclization product 3,3,8,8-tetramethyl-4-*exo*-oxatricyclo[5.2.1.$0^{1,5}$]decane (**93**). It is interesting that the natural terpene α-fenchene(**94**), which is isomeric with **1**, forms under these conditions the same enantiomer of **93**. A possible mechanism is given in Scheme 31 [22].

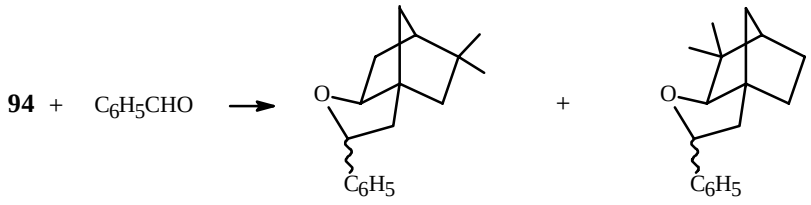


1 **94** **93**

Scheme 31.

It was demonstrated that no reaction occurs in the absence of zeolite and in CH_3COOH:CF_3COOH (5:2 by volume).

We note that benzaldehyde reacts differently than **81** and **84** but analogously to acetone with **94** on β-zeolite to produce a mixture of epimers, 3α- and 3β-phenyl-8,8-dimethyl-4-oxatricyclo[5.2.1.$0^{1,5}$]decanes (**95** and **96**), and an isomer, 3-phenyl-6,6-dimethyl-4-oxatricyclo[5.2.1.$0^{1,5}$]decane (**97**) (Scheme 32).



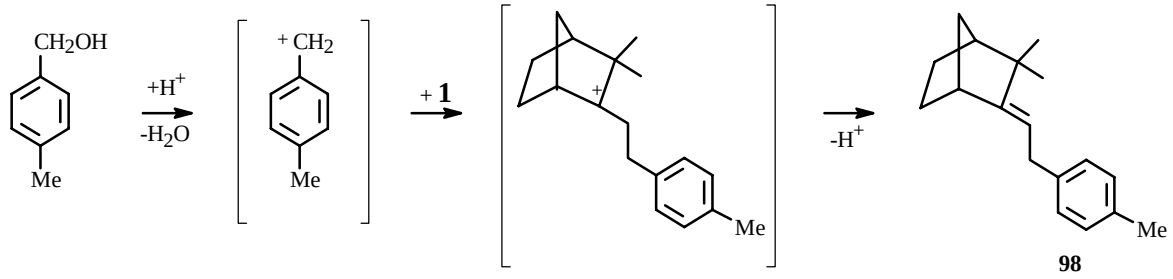
95, 96 **97**

Scheme 32.

REACTIONS OF CAMPHENE AND FATTY-AROMATIC ALCOHOLS WITH PRELIMINARY ELIMINATION OF WATER AND FORMATION OF C-ELECTROPHILES

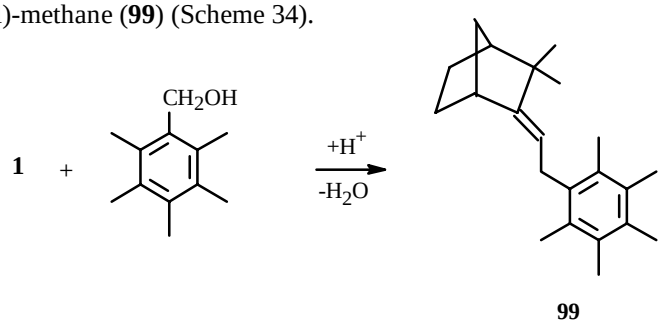
The reaction of **1** with *p*-methylbenzyl alcohol, which is an isomer of *m*-methylbenzyl alcohol, occurs under more forcing conditions, 4 h at 150°C. The reaction follows a different path than that with the *m*-isomer, i.e., with formation of the

racemic hydrocarbon 10-camphenyl-(*p*-tolyl)-methane (**98**) (Scheme 33) [10].



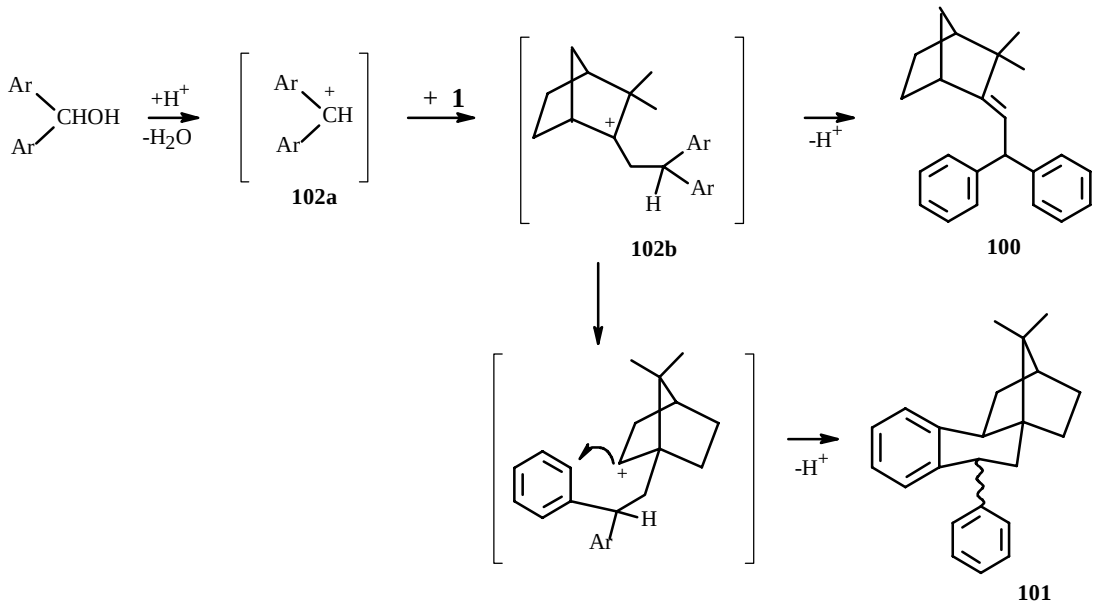
Scheme 33.

Results from experiments with *m*- and *p*-methylbenzyl alcohols indicate that small changes in the reagent structure lead to a change of the reaction path if the reactions are carried out over zeolites. This fact cannot be explained by examining only thermodynamic effects of forming *p*- and *m*-methylbenzyl cations from the corresponding alcohols and hydrocamphene cation (**6**) from **1** because the differences in the energies of formation of the methylbenzyl cations are insignficant. Introducing additional methyl groups into the aromatic ring of *p*-methylbenzyl alcohol enhances formation of the hydrocarbons. Thus, pentamethylbenzyl alcohol reacts with **1** under mild conditions (20°C) to give in 84% yield a compound analogous to **98**, 10-camphenyl-(pentamethylphenyl)-methane (**99**) (Scheme 34).



Scheme 34.

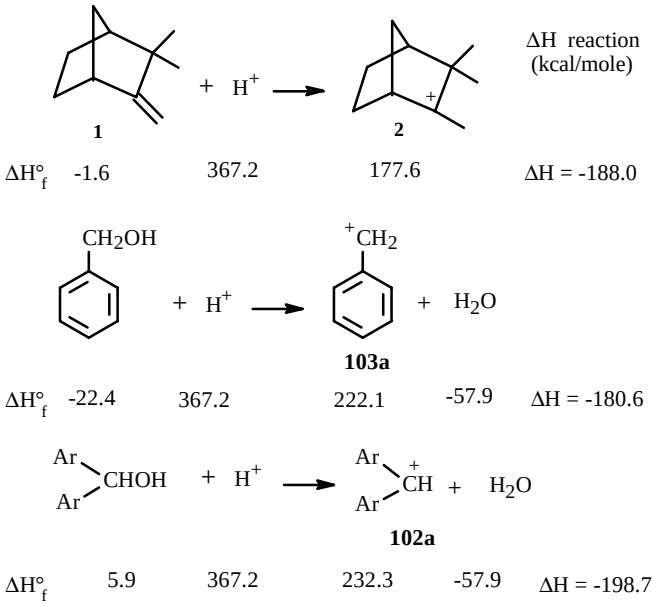
Reaction of benzhydrol and **1** produces the racemic hydrocarbons 10-camphenyldiphenylmethane (**100**) and 11,11-dimethyl-3-phenyl-6-*endo*-H-4,5-benzotricyclo[6.2.1.0^{1,6}]undecane (**101**) in yields of 46 and 12%, respectively [10] (Scheme 35).



Scheme 35.

The electrophilic species in the reactions of **1** with *m*- and pentamethylbenzyl alcohols and benzhydrol is proposed to be not **6** but the cation generated from the alcohol via protonation and dehydration. Obviously, the thermodynamics favor formation of cations from pentamethylbenzyl alcohol and benzhydrol more than from *p*-methylbenzyl alcohol. As a result, the reaction of **1** with the first two alcohols occurs under milder conditions than with *p*-methylbenzyl alcohol. The carbocation (**102b**) generated from benzhydrol first undergoes a WM rearrangement and only then reacts via electrophilic substitution to form the tricyclic product with the isobornyl moiety. A 5,3-shift of H and electrophilic substitution do not occur, as would be expected from the reaction of **1** and benzene and its methyl-substituted derivatives.

The difference in the behavior of benzyl alcohol and benzhydrol in reactions with **1** are explained well by comparing the thermodynamics of formation of hydrocamphene cation (**2**), cation **102a**, and benzylcation **103a**. In the first reaction, formation of **2** is more favorable; in the second, **102a**. This determines whether alkoxylation or aralkylation of **1** occurs (Scheme 36) [10]. The heats of formation of the neutral compounds were calculated using PM3; of carbocations, AM1.



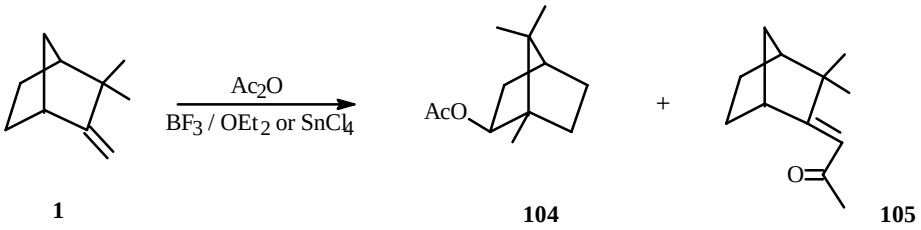
Scheme 36.

REACTION OF CAMPHENE AND ACYLATING AGENTS

The reaction of aromatic compounds [23, 24] and aliphatic and cyclic olefins [25] with acetic anhydride in the presence of zeolites gives the standard acylation products.

Two types of intermolecular processes are possible in the reaction of terpenoids with acetic anhydride over aluminosilicate catalysts. The first involves attack of an acylium-cation on the neutral terpenoid, further transformations of the resulting intermediate, and final formation of the corresponding ketone, an acylation product. The second path should apparently begin with protonation of the terpenoid, then intramolecular arrangements of the resulting cation, and finally capture of the cation by acetic anhydride. In this instance, the final product arises from acetoxylation. The ratio of these paths depends obviously on the ratio of the relative stabilities of the acylium-cation and the cations formed from the terpenoids in the presence of aluminosilicate catalysts. Furthermore, intramolecular rearrangements of the substrate that are catalyzed by acetic anhydride over the catalyst and that do not occur without Ac_2O are possible.

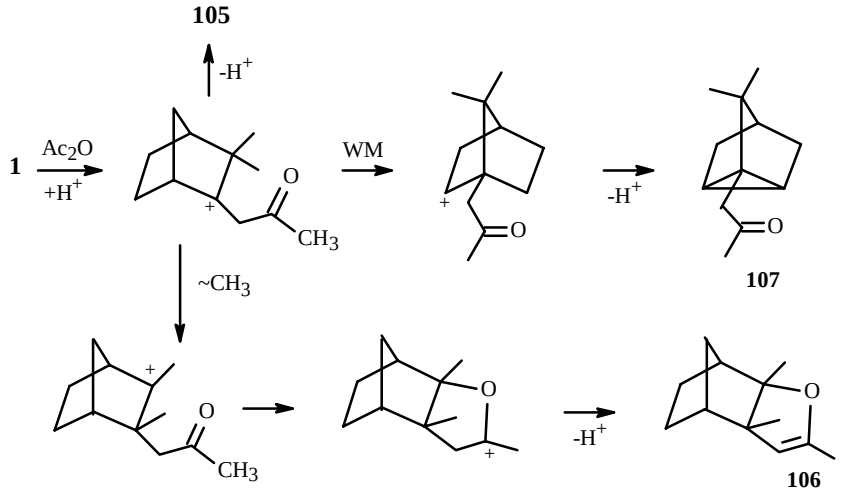
The reaction of **1** with acetic anhydride was previously carried out with Lewis acids. This produced [26] isobornylacetate (**104**) and *ω*-acetylcamphene (**105**) (Scheme 37).



Scheme 37.

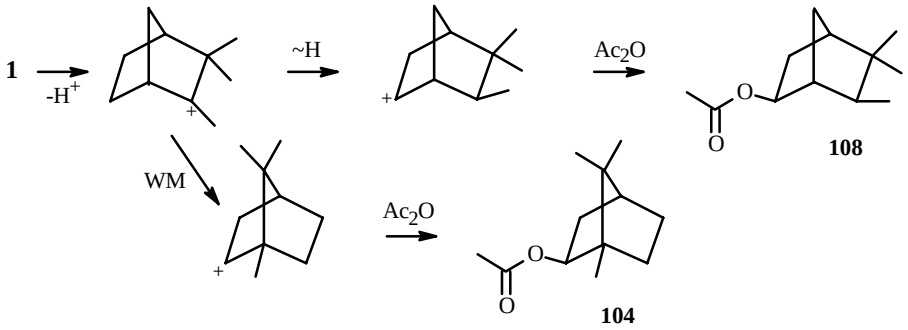
Reaction of **1** with Ac_2O over β-zeolite gives the expected **104** and **105** and 2,4,6-trimethyl-3-oxatricyclo[5.2.1.$0^{2,6}$]dec-4-ene (**106**), 1-(7,7-dimethyltricyclo[2.2.1.$0^{2,6}$]hept-1-yl)-propan-2-one (**107**), and 2,2-dimethyl-3-*exo*-methyl-5-*exo*-acetoxybicyclo[2.2.1]heptane (**108**). The main products were **105** and **106** [27].

Obviously, the reaction follows two paths that differ in mode of generation of the initial carbocations. The first path implies attack of an acylium-cation on the double bond of **1**. Then, the resulting intermediate is either deprotonated to form **105** or further transformed (1,2-methyl shift or WM rearrangement) and only then stabilized by intramolecular hetero- (**106**) or carbocyclization (**107**) (Scheme 38).



Scheme 38.

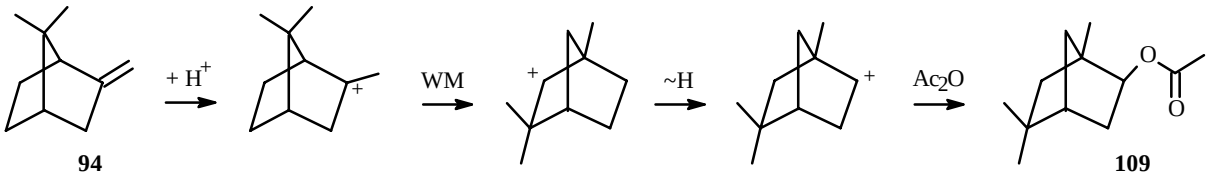
The second path implies initial attack by a proton and then skeletal rearrangement of the resulting hydrocamphene cation **2** or hydride shift in it. The reaction ends with reaction of the intermediates with acetoxy group and forms **104** and **108** (Scheme 39).



Scheme 39.

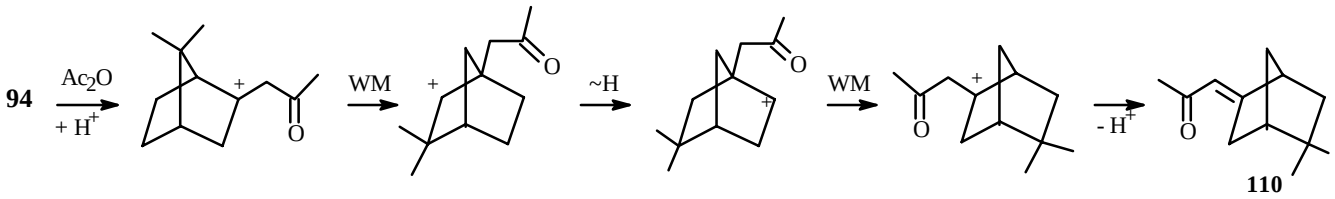
It is interesting that the ratio of acylation and acetoxylation products is ~3:1 whereas either only **104** is formed or the acylation product in very small yield (2%) if Lewis acids are used as catalysts [26]. However, using acetylchloride as the acylating agent over β-zeolite gives results comparable with those reported earlier [26]. The reaction products contain **104** and **105** with a distinct predominance of the acetoxylation product (**104**). The overall product yield for reaction of **1** with acetylchloride is significantly less, 13% vs. 57% for the reaction of **1** and acetic anhydride over β-zeolite. Under homogeneous conditions [26] and depending on the catalyst, the yield was 21-46%. Montmorillonite K-10 was less effective as a catalyst for the above transformations.

The reaction of α-fenchene (**94**), which is isomeric with **1**, and acetic anhydride over zeolite produces 2-*exo*-acetoxy-1,5,5-trimethylbicyclo[2.2.1]heptane (**109**) as the main product and smaller quantities of 1-(5,5-dimethylbicyclo[2.2.1]hept-2-ylidene)-propan-2-one (**110**), the acylation product. Possible formation paths of **109** and **110** are shown in Schemes 39 and 40. We propose initial protonation of **94** and then WM rearrangement, 1,3-hydride shift, and reaction of the resulting carbocation ion with acetic anhydride for the formation of **109** (Scheme 40).



Scheme 40.

For **110**, the reaction apparently begins with attack of acylium-cation on the double bond of **94** (Scheme 41) with subsequent WM rearrangement, 1,3-hydride shift, and another WM rearrangement. Deprotonation of the resulting cation leads to **110**.



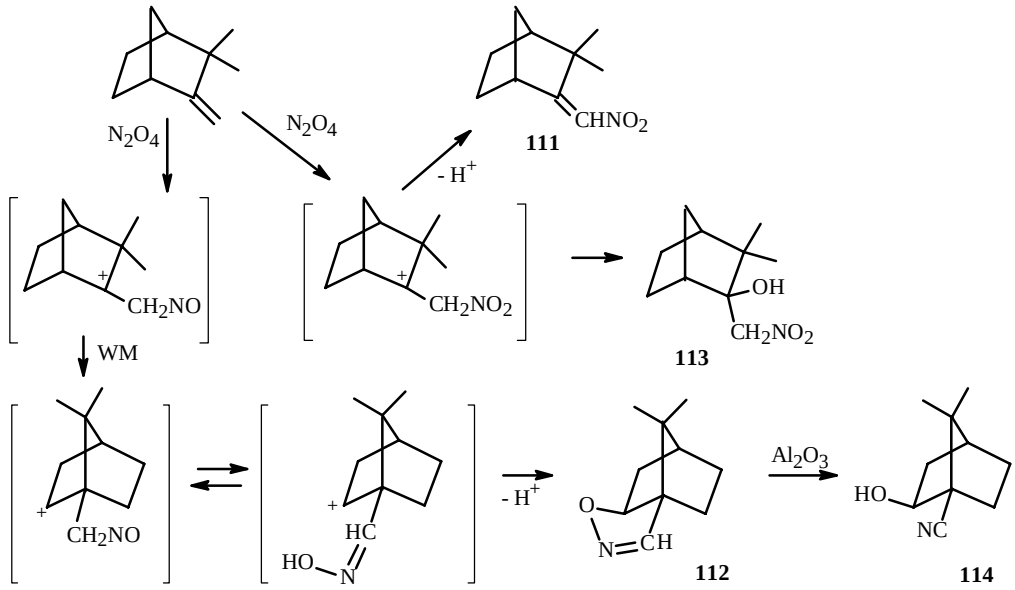
Scheme 41.

Schemes 38 and 41 show that **1** and **94** in the presence of heterogeneous β-zeolite catalyst undergo extensive mutlistep transformations that form unexpected compounds not observed under homogeneous conditions.

The above reactions of **1** do not occur without catalyst or with acetic acid as catalyst.

REACTIONS OF CAMPHENE AND HETEROCATIONS (NO_2^+, NO^+)

In conclusion, let us examine reactions of **1** with nitrating agents. Reaction of **1** and N_2O_4 in CH_2Cl_2 in the presence of β-zeolite gave a mixture of ω-nitrocamphene (**111**) (18% yield) and the unusual product of nitrosylation, 10,10-dimethyl-3-aza-4-oxatricyclo[5.2.1.$0^{1,5}$]dec-2-ene (**112**) (51%) in a 1:4.4 ratio (GLC). If the reaction is performed under these same conditions but in the presence of medium-pore zeolite ZSM-5 or narrow-pore erionite, the results are essentially the same. Compounds **111** and **112** are formed in ratios of 1:4.2 and 1:4.4, respectively. Using wide-pore β-zeolite as catalyst but in diethylether gives **111** and **112** in addition to the nitro derivative **113** (Scheme 42) in a 1.7:1:2.5 ratio (GLC) and yields of 9, 18, and 12%, respectively. We note that the last product was, according to the literature [28], the principal one for reaction of **1** and N_2O_4 in diethylether. Performing the reaction of **1** and N_2O_4 without zeolite in CH_2Cl_2 gives **112** and **111** in a 1.8:1 ratio. If this same reaction occurs in diethylether, the reaction mixture contains **111** and **113** (~1:3). Compound **112** is not observed [28].



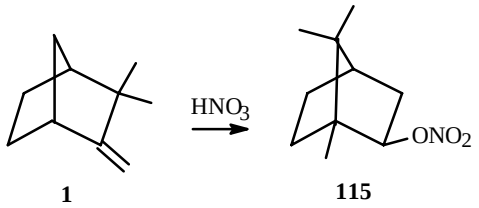
Scheme 42.

Compound **112** on storage, or faster on passage over a column of Al_2O_3, transforms into 2-*exo*-hydroxy-1-cyano-7,7-dimethylnorbornane (**114**). Storing pure **112** and N_2O_4 over β-zeolite produces a mixture of the starting compound and the isomerization product **114** in a 1:5 ratio. Nitro-olefin **111** was not observed.

Reaction of **1** and N_2O_4 did not produce **112** and **114** [28]. In reactions with olefins, N_2O_4 acts usually as a nitrating agent. We could find no information on the use of N_2O_4 as a nitrosylating agent for olefins. Compound **112** was prepared earlier under typical nitrosylating conditions, reaction of **1** and HNO_2 generated in situ from $NaNO_2$ and H_2SO_4 [30]. This reaction (Scheme 42) involves multistep formation of **112** including addition of NO^+ (or NO) to the double bond, WM rearrangement, isomerization of the nitroso derivative into an oxime, intramolecular alkylation, and proton loss. According to the literature [30], **112** is formed from **1** only under very specific reaction conditions. It is not obtained from reaction with $NaNO_2$+AcOH, N_2O_3, or reduction of **111** by Zn+AcOH.

The ratio of nitrosylation and nitration products is maximal for the reaction in CH_2Cl_2 over zeolite. It should be noted that varying the channel size of the zeolite (erionite, β-zeolite, or ZSM-5) and the modulus (ZSM-12 and β-zeolite) does not significantly change the ratio of nitrosylation and nitration products. This suggests that the role of the zeolite consists of transforming the starting N_2O_4 on the zeolite surface.

In contrast with the described process, reaction of **1** and 69% HNO_3 depends little on the presence of zeolite. The yield of the main product, isobornylnitrate (**115**), is 60-80%. The highest yield and selectivity are found for reactions using β-zeolite (Scheme 43).



Scheme 43.

Thus, carbocations, protons, acylium-cations, or heterocations can act as electrophiles in the reaction of **1**, one of the most common natural monoterpenes, with electrophiles in the presence of heterogeneous catalysts. The hydrocamphene cation formed from camphene or its derivatives undergo intramolecular rearrangements. Then, the carbocation in the monoterpene is stabilized by either an intramolecular interaction with a nucleophilic center of the species added in the first step (α,β-unsaturated carbonyls, N_2O_4) or an intermolecular reaction with a nucleophile (aromatic hydrocarbons, fatty-aromatic alcohols,

phenols, acetic anhydride). The observed transformations open new synthetic capabilities for using camphene and, probably, other monoterpenes in heterogeneous catalysis.

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