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Reactions of (+)-α-Fenchene and (–)-Camphene with Acetone and Benzaldehyde over β-Zeolite

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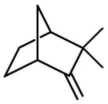
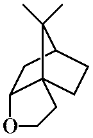
Abstract—Reactions of (+)-α-fenchene and (–)-camphene with acetone and benzaldehyde over β-zeolite lead to formation of tricyclic ethers. Possible reaction mechanisms and solvent effect on these processes are discussed.

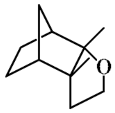
We previously studied reactions of camphene (**I**) over zeolite catalysts with various carbonyl compounds and found that their results strongly depend on the structure of the latter. In particular, camphene (**I**) reacts with formaldehyde over wide-pore β-zeolite to afford tricyclic ethers **II** and **III**; with α-methylacrolein, tricyclic aldehyde **IV** was obtained; and the reaction of **I** with acrolein gave product **V** as a result of replacement of the vinyl hydrogen atom in the former [1]. Likewise, ketone **VI** was formed from camphene (**I**) and methyl vinyl ketone [1].



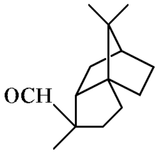
I



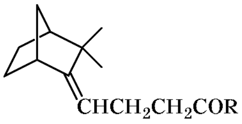
II



III



IV



V, VI

V, R = H; **VI**, R = CH_3.

We have found that camphene (**I**, $[\alpha]_{580}^{20}$ = –60°, *c* = 1, $CHCl_3$) reacts with acetone over β-zeolite in a way different from the reaction with methyl vinyl ketone, yielding optically active heterocyclization product **VII** ($[\alpha]_{580}^{20}$ = –25.2°, *c* = 2, $CHCl_3$). Another natural terpene, α-fenchene (**VIII**, $[\alpha]_{580}^{20}$ = +19.4°, *c* = 1, $CHCl_3$) which is isomeric to **I**, reacted with acetone to afford the same enantiomer of **VII**. Scheme 1 shows possible mechanisms of these transformations. Obviously, in both cases the reaction begins with attack by protonated acetone on the double bond in **I** or **VIII**; the subsequent Wagner–Meerwein (WM) and double Wagner–Meerwein (DWM) rearrangements followed by heterocyclization lead to formation of the final product.

We also examined the effects of the solvent and catalyst on the yield and optical purity of product **VII** in the reaction of α-fenchene (**VIII**) with acetone (20 h, 20°C). In the system $CH_3COOH–CF_3COOH$ (5 : 2, by volume, 20°C) in the absence of a catalyst only tarring occurred. The results are summarized in Table 1. In going from methylene chloride to benzene

Table 1. Reaction of α-fenchene with acetone in various solvents

Solvent, ml	**VIII**, mg	Me_2CO, mg	Yield of **VII**, %	$[\alpha]_{580}^{20}$ ($CHCl_3$)
CH_2Cl_2, 3	131	279	75 (40)	–21.3
CH_2Cl_2–PhH (1 : 1), 4	135	280	68[a] (35)	–17.1
Acetone, 3	119		35 (21)	–3.4
Benzene, 3	118	251	28 (17)	–4.2
No solvent	123	340	62 (35)	–3.4

[a] *exo*-Isofenchyl alcohol **IX**, 12 mg (6%), was also isolated.

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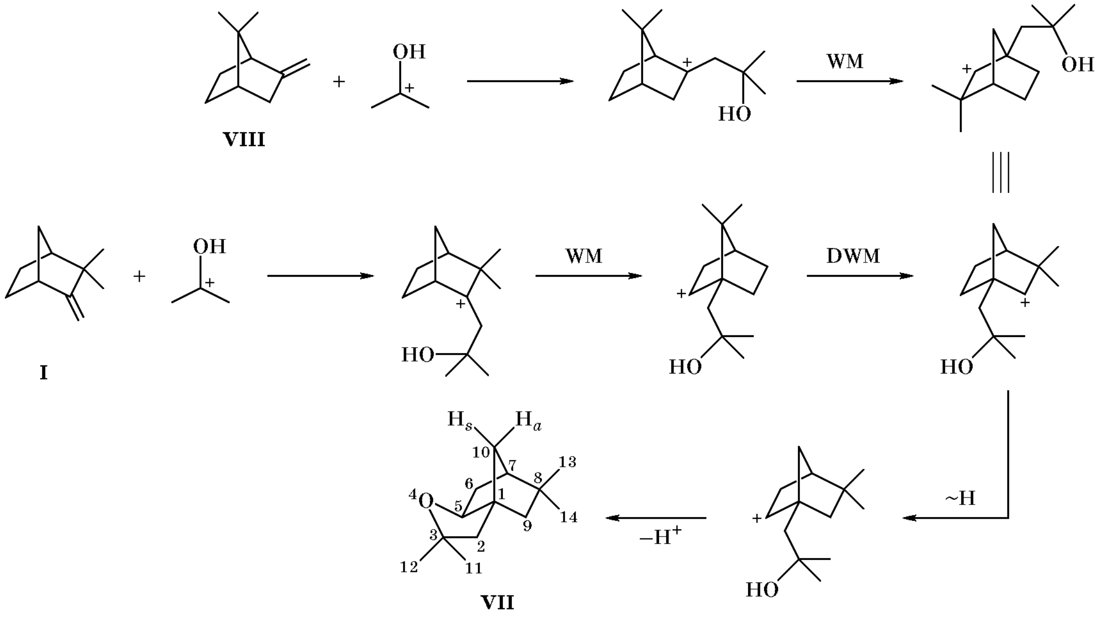
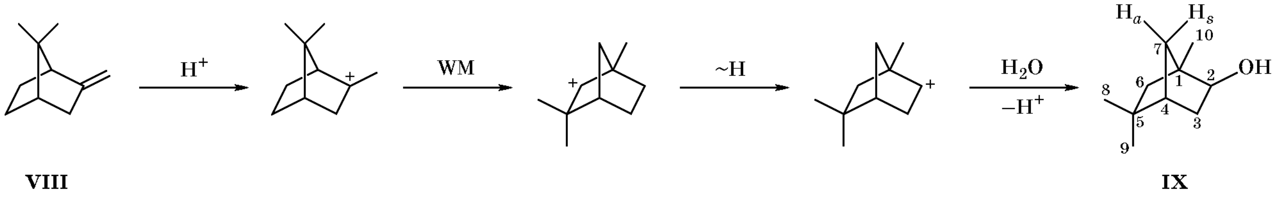
Scheme 1.



Scheme 2.



or acetone the yield of the target product decreases in parallel with its optical activity. These data suggest that the rate of processes leading to racemization and tarring remains sufficiently high, while the rate of formation of product **VII** decreases.

When the reaction of **VIII** with acetone was carried out in a mixture of benzene with methylene chloride, apart from product **VII** we isolated a small amount of *exo*-isofenchyl alcohol (**IX**). The latter was formed as a result of protonation of the double bond in **VIII** (Scheme 2), subsequent rearrangements of the cation thus formed, and addition of external nucleophile.

The reaction of α-fenchene (**VIII**) with benzaldehyde over β-zeolite follows a different pathway, as compared to the reaction of **I** with acrolein and α-methylacrolein, but the pattern is analogous to the reaction with acetone. The products were a mixture of epimers **X** and **XI** and isomeric compound **XII** (Scheme 3). Compounds **X** and **XI** were also formed in the reaction of camphene (**I**) with benzaldehyde, but in a very poor yield (GLC).

The structure of the products was proved by ^{1}H and ^{13}C NMR spectroscopy. The *endo*-orientation of the 5-H proton in **VII**, **X**, and **XI** follows from the vicinal

Scheme 3.

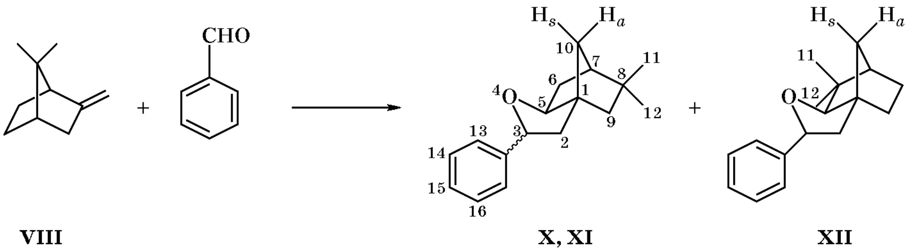


Table 2. ^{13}C NMR spectra of compounds **VII** and **X**–**XII**, δ_C, ppm

Atom no.	**VII**	**X**	**XI**	**XII**
1	57.95 s	58.20 s	57.00 s	58.01 s
2	42.90 t	39.70 t	37.85 t	39.06 t
3	83.16 s	81.91 d	82.98 d	82.64 d
5	83.68 d	85.97 d	86.29 d	96.04 d
6	34.26 t	35.80 t	33.87 t	43.46 s
7	49.76 d	49.31 d	49.73 d	49.44 d
8	36.89 s	36.86 s	36.86 s	24.47 t
9	46.04 t	45.01 t	45.61 t	27.83 t
10	40.71 t	39.13 t	41.46 t	40.20 t
11	30.65[a] q	30.94 q	31.02 q	23.24 q
12	29.54[a] q	26.74 q	26.74 q	26.10 q
13	31.06 q	144.80 s	143.57 s	144.85 s
14	26.71 q	125.24 d	125.76 d	125.58 d
15		128.24 d	128.19 d	128.26 d
16		126.85 d	126.93 d	126.94 d

[a] Alternative assignment is possible.

spin–spin coupling constants with *exo*-6-H and *endo*-6-H, the presence of *W*-coupling with *anti*-10-H, and the absence of such coupling with *exo*-9-H. The *endo* orientation of 5-H in molecule **XII** is confirmed by analysis of only long-range *W*-coupling constants, and the orientation of 2-H in compound **IX** was derived from analysis of vicinal coupling constants with two 3-H protons and long-range coupling with *exo*-6-H.

The signals from geminal methyl groups in the ^{13}C NMR spectra of compounds **VII** and **IX**–**XII** were assigned by comparing the corresponding chemical shifts with those reported in [2] for related structures, and their ^1H NMR signals were assigned on the basis of two-dimensional ^{13}C–^1H correlation spectra using direct coupling constants. The ^{13}C NMR spectrum of **IX** concided with that given in [3]; its ^1H NMR spectrum was also reported [3], but our data are more complete.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer at 400.13 and 100.61 MHz, respectively, from samples dissolved in CCl_4–$CDCl_3$ (1 : 1, by volume); the chemical shifts were measured relative to the solvent (chloroform) signals, δ 7.24, δ_C 76.90 ppm. The signals were assigned by analysis of geminal, vicinal, and long-range coupling constants in the ^1H–^1H double-resonance spectra and by analysis of the ^{13}C NMR spectra using off-resonance technique, two-dimensional ^{13}C–^1H correlation on direct coupling constants (COSY, $^1J_{CH}$ = 135 Hz), and unidimensional ^{13}C–^1H correlation on long-range coupling constants (LRJMD, J_{CH} = 10 Hz). The ^{13}C chemical shifts of compounds **VII** and **X**–**XII** are given in Table 2. The high-resolution mass spectra were run on a Finnigan MAT 8200 mass spectrometer, and the GC–MS data were obtained on an HP G1800A instrument. The optical rotations were measured using a Polamat A spectropolarimeter from solutions in $CHCl_3$.

The purity of the initial compounds and final products was checked by GLC on a Model 3700 chromatograph equipped with a flame-ionization detector and a 17000 × 0.25-mm glass capillary column (stationary phase VC-30); oven temperature 60–190°C; carrier gas helium, inlet pressure 2 atm.

β-Zeolite (H^+ form) was prepared by the procedure described in [4]; [Si]/[Al] ratio 40, pore size 0.75–0.8 nm, oxide weight fractions, %: Na_2O (0.04), Al_2O_3 (5.14), SiO_2 (81.57). The catalyst was calcined for 2 h at 500°C just before use. The solvents were purified by passing through a column charged with calcined aluminum oxide. The products were isolated by column chromatography on silica gel (40–100 μm) using solutions of ether in hexane (0 to 5% of the former) as eluent.

Reaction of camphene (I) with acetone. A solution of 151 mg of camphene (**I**) and 320 mg of acetone in 2 ml of CH_2Cl_2 was added dropwise to a mixture of 150 mg of β-zeolite and 1 ml of CH_2Cl_2. The mixture was stirred for 20 h at room temperature, the products were extracted into diethyl ether, the extract was evaporated, and the residue was subjected to column chromatography to isolate 16 mg (7%) of 3,3,8,8-tetramethyl-*exo*-4-oxatricyclo[5.2.1.0^{1,5}]decane (**VII**), $[\alpha]^{20}_{580}$ = +5° (*c* = 1.5). ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.90 s ($C^{14}H_3$), 0.91 d.d (*endo*-9-H, $J_{endo\text{-}9,exo\text{-}9}$ = 12, $J_{endo\text{-}9,syn\text{-}10}$ = 3), 0.97 s ($C^{13}H_3$), 1.18 s and 1.28 s ($C^{11}H_3$, $C^{12}H_3$), 1.40 d (*exo*-9-H, *J* = 12), 1.42 d.d.d (*exo*-6-H, $J_{exo\text{-}6,endo\text{-}6}$ = 13, $J_{exo\text{-}6,7}$ = 3.5, $J_{exo\text{-}6,endo\text{-}5}$ = 3), 1.42 m (*anti*-10-H), 1.54 d.d.d (*syn*-10-H, $J_{syn\text{-}10,anti\text{-}10}$ = 10, $J_{syn\text{-}10,endo\text{-}9}$ = 3, $J_{syn\text{-}10,7}$ = 1.2), 1.60 d and 1.73 d (2H, 2-H, *J* = 12.5, *AB* system), 1.73 br.d (7-H, *J* = 3.5), 1.99 d.d.d.d (*endo*-6-H, *J* = 13, $J_{endo\text{-}6,endo\text{-}5}$ = 7, $J_{endo\text{-}6,anti\text{-}10}$ = 3, $J_{endo\text{-}6,7}$ = 0.5), 3.67 d.d.d (*endo*-5-H, *J* = 7, 3, $J_{endo\text{-}5,anti\text{-}10}$ = 1.2). Mass spectrum, *m*/*z* (I_{rel}, %): 194.1 (5) $[M]^+$, 179.1 (100), 161.1 (15), 138.1 (12), 123.1 (15), 121.1 (31), 107.1 (11), 93

(16), 80.1 (19), 69 (10), 55 (10), 43 (21). Found *M*: 194.16681. $C_{13}H_{22}O$. Calculated *M*: 194.16706.

Reaction of α-fenchene (VIII) with acetone. A solution of α-fenchene (**VIII**) in acetone was added dropwise to 150 mg of β-zeolite wetted with appropriate solvent (Table 1). The mixture was stirred for 20 h at room temperature, the products were extracted into diethyl ether, the extract was evaporated, and the residue was subjected to column chromatography. The results are summarized in Table 1.

^{1}H NMR spectrum of compound **IX**, δ, ppm (*J*, Hz): 0.77 br.d (*endo*-6-H, $J_{endo\text{-}6,\,exo\text{-}6}$ = 12), 0.90 s (C^9H_3), 0.98 s (C^8H_3), 1.01 s ($C^{10}H_3$), 1.14 d (*exo*-6-H, *J* = 12), 1.15 d.d.d (*exo*-3-H, $J_{exo\text{-}3,\,endo\text{-}3}$ = 14, $J_{exo\text{-}3,\,4}$ = 4.5, $J_{exo\text{-}3,\,endo\text{-}2}$ = 3.5), 1.34–1.40 m (2H, 7-H), 1.59 br.d (4-H, *J* = 4.5), 2.17 d.d.m (*endo*-3-H, *J* = 14, $J_{endo\text{-}3,\,endo\text{-}2}$ = 7), 3.32 br.d.d (*endo*-2-H, *J* = 7, 3.5).

Reaction of α-fenchene (VIII) with benzaldehyde. Benzaldehyde, 200 mg, was added to a mixture of 400 mg of β-zeolite and 10 ml of CH_2Cl_2, and a solution of 150 mg of α-fenchene and 200 mg of benzaldehyde in 3 ml of CH_2Cl_2 was then added dropwise. The mixture was stirred for 40 min, the products were extracted into diethyl ether, the extract was evaporated, and the products were separated by repeated column chromatography on silica gel. We isolated 46 mg of a mixture of 8,8-dimethyl-3α(β)-3β(α)-phenyl-*exo*-4-oxatricyclo[5.2.1.0^{1,5}]decanes **X** and **XI** at a ratio of 7 : 3 (overall yield 17%), $[\alpha]^{20}_{580}$ = +5° (*c* = 1.5) (found *M*: 242.16734; $C_{17}H_{22}O$; calculated *M*: 242.16706); 11 mg (4%) of 6,6-dimethyl-3-phenyl-*exo*-4-oxatricyclo[5.2.1.0^{1,5}]decane (**XII**); and 41 mg of a mixture containing (according to the GC–MS data), 12% of β-fenchene, 23% of α-fenchene, and 40% of α-fenchene dimerization products (total of 8 substances).

^{1}H NMR spectrum of compound **X**, δ, ppm (*J*, Hz): 0.95 s ($C^{12}H_3$), 0.99 d.d (*endo*-9-H, $J_{endo\text{-}9,\,exo\text{-}9}$ = 12, $J_{endo\text{-}9,\,syn\text{-}10}$ = 3), 1.04 s ($C^{11}H_3$), 1.52 d (*exo*-9-H, *J* = 12), 1.53 m (*exo*-6-H, $J_{exo\text{-}6,\,endo\text{-}6}$ = 13, $J_{exo\text{-}6,\,7}$ = 4, $J_{exo\text{-}6,\,endo\text{-}5}$ = 3), 1.54 m (*anti*-10-H), 1.63 d.d.d (*syn*-10-H, $J_{syn\text{-}10,\,anti\text{-}10}$ = 10, $J_{syn\text{-}10,\,endo\text{-}9}$ = 3, $J_{syn\text{-}10,\,7}$ = 1.2), 1.77 d.d (2-H, $J_{2,2'}$ = 12.5, $J_{2,3}$ = 9), 1.83 br.d (7-H, *J* = 4), 2.14 d.d.d (*endo*-6-H, *J* = 13, $J_{endo\text{-}6,\,endo\text{-}5}$ = 6.5, $J_{endo\text{-}6,\,anti\text{-}10}$ = 3), 2.33 d.d (2′-H, *J* = 12.5, $J_{2',3}$ = 6.5), 3.95 d.d.d (*endo*-5-H, *J* = 6.5, 3, $J_{endo\text{-}5,\,anti\text{-}10}$ = 1), 5.22 d.d (3=H, *J* = 9, 6.5), 7.15–7.30 m (5H, H_{arom}).

^{1}H NMR spectrum of compound **XI**, δ, ppm (*J*, Hz): 0.96 s ($C^{12}H_3$), 1.01 s ($C^{11}H_3$), 1.04 m (*endo*-9-H), 1.52 d (*exo*-9-H, $J_{exo\text{-}9,\,endo\text{-}9}$ = 12), 1.46–1.64 m (2H, 10-H), 1.65 d.d.d (*exo*-6-H, $J_{exo\text{-}6,\,endo\text{-}6}$ = 13, $J_{exo\text{-}6,\,7}$ = 3.5, $J_{exo\text{-}6,\,endo\text{-}5}$ = 3), 1.79 br.s (7-H), 1.84 d.d (2-H, $J_{2,2'}$ = 12.5, $J_{2,3}$ = 6), 2.10 d.d.d (*endo*-6-H, *J* = 13, $J_{endo\text{-}6,\,endo\text{-}5}$ = 6.5, $J_{endo\text{-}6,\,anti\text{-}10}$ = 3), 2.22 d.d (2′-H, *J* = 12.5, $J_{2',3}$ = 9), 3.75 d.d.d (*endo*-5-H, *J* = 6.5, 3, $J_{endo\text{-}5,\,anti\text{-}10}$ = 1), 5.04 d.d (3-H, *J* = 9, 6), 7.15–7.35 m (5H, H_{arom}).

Compound **XII**. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.05 s ($C^{11}H_3$, $C^{12}H_3$), 1.09 d.d.d (*anti*-10-H, $J_{anti\text{-}10,\,syn\text{-}10}$ = 10, $J_{anti\text{-}10,\,endo\text{-}5}$ = 1.5, $J_{anti\text{-}10,\,7}$ = 1.5), 1.25 m (*endo*-8-H), 1.45 d.d.d.d (*exo*-8-H, $J_{exo\text{-}8,\,endo\text{-}8}$ = 13, $J_{exo\text{-}8,\,exo\text{-}9}$ = 13, $J_{exo\text{-}8,\,7}$ = 4.5, $J_{exo\text{-}8,\,endo\text{-}9}$ = 3.5), 1.63–1.74 m (2H, 9-H), 1.76 d.m (7-H, *J* = 4.5), 1.80 d.d (2-H, $J_{2,2'}$ = 12.5, $J_{2,3}$ = 9), 1.97 d.m (*syn*-10-H, *J* = 10), 2.24 d.d (2′-H, *J* = 12.5, $J_{2',3}$ = 6.5), 3.44 d (*endo*-5-H, $J_{endo\text{-}5,\,anti\text{-}10}$ = 1.5), 5.16 d.d (3-H, *J* = 9, 6.5), 7.17 quint and 7.26 d (5H, H_{arom}, AB_4 system). Mass spectrum, *m*/*z* (I_{rel}, %): 242.1 (37) $[M]^+$, 213 (39), 151 (20), 138.1 (47), 136.1 (46), 123.1 (27), 121.1 (21), 109.1 (51), 105 (100), 95 (37), 93 (19), 91 (41), 80 (30.51) 77 (37), 69 (20), 67 (19), 55 (16), 43.1 (14), 41 (32), 39 (10), 28 (37). Found *M*: 242.16685. $C_{17}H_{22}O$. Calculated *M*: 242.16706.

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