ISSN 1070-4280, Russian Journal of Organic Chemistry, 2007, Vol. 43, No. 4, pp. 511–517. © Pleiades Publishing, Ltd., 2007.
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Synthesis of Epoxy Dinitriles from Citral and Their Acid-Catalyzed Transformations

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Received March 13, 2006

Abstract—2,3- and 6,7-Epoxy derivatives of citral react with malononitrile in the presence of basic Csβ-zeolite to give the corresponding epoxyalkenylidenemalononitriles as the major products. Epoxy dinitriles obtained from 6,7-epoxycitral undergo acid-catalyzed transformations into tetrahydrofuran derivatives or acyclic polyenes containing hydroxy and cyano groups, depending on the catalyst nature.

DOI: 10.1134/S1070428007040045

Wide application of heterogeneous catalysts, including basic zeolites, in fine organic synthesis constitutes an important line in the development of modern organic chemistry [1, 2]. We previously showed [3, 4] that basic Cs-exchanged β-zeolite (Csβ) effectively catalyzes reactions of α,β-unsaturated carbonyl compounds of the terpene series with CH acids. These transformations occurred at room temperature in the presence of a catalytic amount of zeolite, and the latter can be reused without loss in catalytic activity; the yields were relatively good, taking into account the complex substrate structure. For example, the reaction of widespread monoterpenoid citral (**Ia/Ib**, a 1:1 mixture of the *E* and *Z* isomers) with malononitrile in the presence of basic Csβ-zeolite under mild conditions led to the formation of a mixture of dinitriles **IIa** and **IIb** at a ratio of 1:1 in 41% yield (Scheme 1) [3].

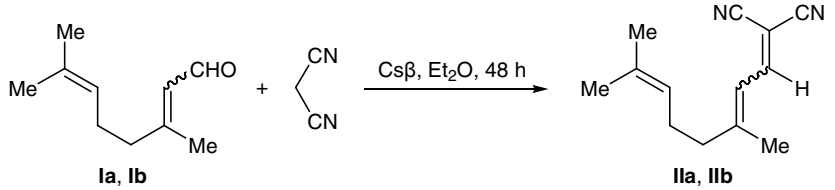
It is known that Knoevenagel reactions of citral in the presence of common catalysts often take several pathways, leading to the formation of mixtures of products [5, 6]. The smooth reaction of citral with malononitrile catalyzed by Csβ prompted us to use as substrates more labile citral derivatives, 2,3- and 6,7-epoxycytrals, with a view to obtain new oxygen-containing polyfunctional compounds and extend concepts on organic reaction mechanisms.

We have found that 2,3-epoxy citral derivatives **IIIa/IIIb** (a mixture of the *E* and *Z* isomers at a ratio of ~1.2:1) react with malononitrile in diethyl ether at room temperature in the presence of Csβ (reaction time 2 h) to give mainly a mixture of dinitriles **IVa** and **IVb** in an overall yield of 47% (*E*/*Z*-isomer ratio ~1.3:1), the oxirane ring remaining intact (Scheme 2).

The only example of the Knoevenagel reaction of malononitrile with α,β-epoxy aldehyde, occurring with retention of the epoxide ring, was reported in [7]; in this case, the reaction was carried out in the presence of a mixture of ammonium acetate and acetic acid; this catalyst is used most frequently in the Knoevenagel condensations. Aldehyde **VI** reacted with malononitrile to afford 35% of the corresponding epoxy dinitrile **VII** (Scheme 2).

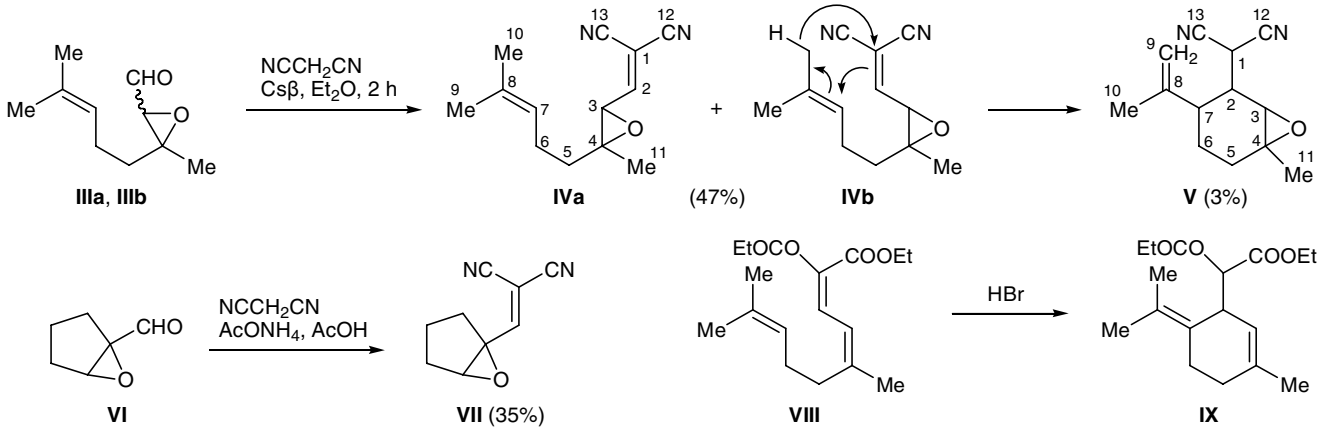
The use of Csβ as catalyst ensures much simpler procedure for the treatment of reaction mixtures ob-

Scheme 1.



Ia, **Ib** **IIa**, **IIb**

Scheme 2.



tained from epoxy aldehydes and malononitrile, only a catalytic amount of Csβ is necessary, and the catalyst can readily be regenerated. Therefore, the proposed catalytic system is clearly more advantageous.

In the reaction of 2,3-epoxy citral derivatives **IIIa** and **IIIb** with malononitrile in the presence of Csβ, apart from epoxy dinitriles **IVa** and **IVb**, we isolated a small amount of bicyclic compound **V** (yield 3%); obviously, it was formed by cyclization of isomer **IVb** (Scheme 2). An analogous cyclization of citral derivatives into compounds having a *p*-menthane skeleton was observed under conditions of photochemical activation [8], as well as in acidic media; for example, diester **IX** was synthesized from compound **VIII** by the action of HBr [9] (Scheme 2). However, the occurrence of such cyclization in the presence of a basic catalyst under mild conditions seems to be quite surprising. Presumably, the acid-catalyzed cyclization path with conservation of the epoxy group in the transformation of epoxy dinitriles **IVa** and **IVb** into compound **V** is hardly probable, taking into account easy opening of epoxide ring in acid medium.

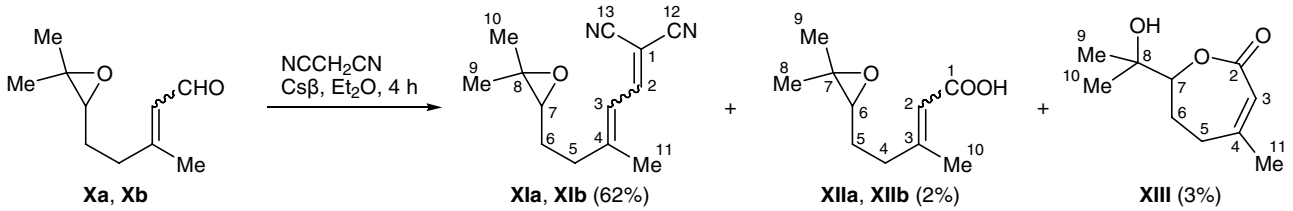
Likewise, 6,7-epoxy derivatives **Xa/Xb** (a mixture of the *E* and *Z* isomers at a ratio of ~1.2:1) reacted with malononitrile in diethyl ether at room temperature in the presence of Csβ (reaction time 4 h) to give the corresponding isomeric epoxy dinitriles **XIa/XIb** ($E:Z \approx 1.7:1$) as the major products; in addition, small amounts of isomeric epoxy acids **XIIa/XIIb** ($E:Z \approx 1:0.6$) and lactone **XIII** were isolated (Scheme 3). Lactone **XIII** can be formed only from *Z* isomer **XIIb**.

Presumably, epoxy acids **XIIa/XIIb** are formed from 6,7-epoxy citrals **Xa/Xb** as a result of oxidation, e.g., with atmospheric oxygen. The subsequent intramolecular cyclization of *Z* isomer **XIIb** gives lactone **XIII**. To verify this assumption, compounds **Xa/Xb** were kept over Csβ without a solvent for 8 days. After appropriate treatment, we isolated a mixture containing initial 6,7-epoxy citrals **Xa/Xb** and compound **XIII** (Scheme 4) at a ratio of 7:1 (according to the ^{1}H NMR data). The calculated conversion of the initial epoxy aldehyde was 36%, and the yield of lactone **XIII** calculated on the reacted **Xa/Xb** was 26%.

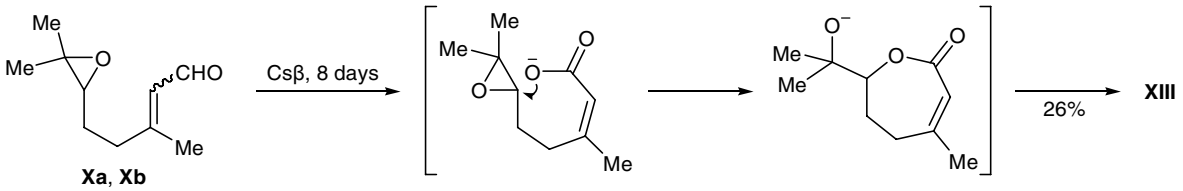
Thus we showed that reactions of epoxy aldehydes with malononitrile in the presence of Cs-exchanged β-zeolite occur with conservation of the epoxy group and lead to the formation of the corresponding epoxy dinitriles in fairly good yields.

Polyfunctional compounds **IVa/IVb** and **XIa/XIb** possess an epoxide moiety which should make them quite reactive in acid medium. Therefore, we examined the behavior of epoxy dinitriles **IVa/IVb** and **XIa/XIb** in homogeneous and heterogeneous acid media with a view to compare the results with our previous data

Scheme 3.



Scheme 4.

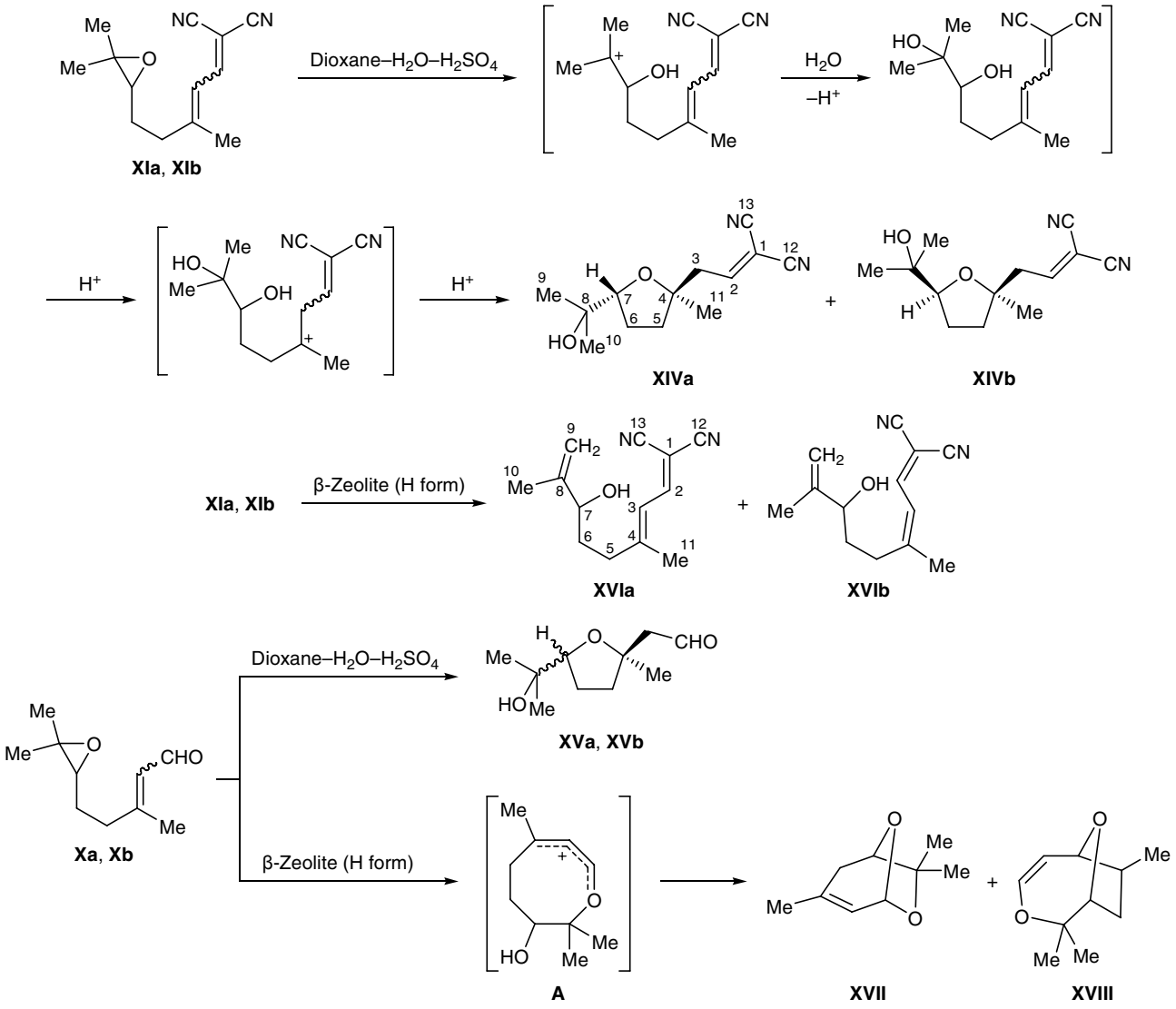


[10–12] on the transformations of 2,3- and 6,7-epoxy citrals in various acid media and estimate the effect of functional substitution on the transformation pathways.

When isomer mixture **IVa/IVb** was kept in the system dioxane–water–sulfuric acid (homogeneous) or over solid acid catalysts (β-zeolite, askanite–bentonite clay), complex mixtures of unidentifiable products were obtained, and the reactions were accompanied by strong tarring. Analogous results were obtained by us previously with 2,3-epoxy derivatives of citral in the presence of various acid catalysts (the main tansformation pathway was polymerization of the initial compounds) [11].

From epoxy dinitriles **XIa/XIb** in the system dioxane–water–sulfuric acid we obtained isomeric substituted tetrahydrofurans **XIVa** and **XIVb** in an overall

Scheme 5.



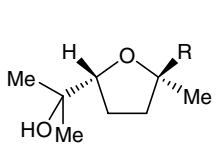
yield of 18% (Scheme 5). According to the GLC data, isomer **XIVb** predominated in the reaction mixture (**XIVa**:**XIVb** ≈ 1:1.5); after separation by column chromatography, the major isomer was **XIVa** (ratio **XIVa/XIVb** ≈ 1:0.6). Presumably, compound **XIVb** undergoes decomposition during chromatographic separation; its instability may be responsible (at least partially) for the poor yield of the isolated products. Analogous transformations into tetrahydrofuran derivatives **XVa/XVb** (Scheme 5) were observed by us previously while studying the behavior of 6,7-epoxy compounds **Xa/Xb** in acid medium [12].

A probable scheme of the formation of compounds **XIVa** and **XIVb** from epoxy dinitriles **XIa** and **XIb** includes protonation and opening of the oxirane ring in the substrate, addition of water molecule to the resulting cation, protonation of intermediate diol, and heterocyclization (Scheme 5). A similar mechanism was proposed by us previously to rationalize the formation of compounds **XVa** and **XVb** [12]. Unlike 6,7-epoxy isomers **Xa/Xb**, protonation of the intermediate diols derived from **XIa/XIb** could give rise to either tertiary or allylic cationic center. However, judging by the product structure, only the tertiary rather than secondary allylic cation is formed in our case.

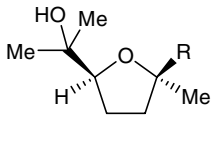
The transformation of isomeric epoxy dinitriles **XIa/XIb** over acid β-zeolite involved opening of the oxirane ring to give compounds **XVIa** and **XVIb** (Scheme 5) at a ratio of 1:4.2 in an overall yield of 17%, the conversion being 67%; the unchanged *E* isomer was mainly recovered from the reaction mixture, and the process was accompanied by considerable tarring. Under analogous conditions, from 6,7-epoxy derivatives **Xa/Xb** we previously [12] isolated exclusively bicyclic ethers **XVII** and **XVIII** (Scheme 5), while no hydroxy polyenes were detected.

Thus replacement of the aldehyde carbonyl oxygen atom in **Xa/Xb** by dicyanomethylidene group in going to epoxy dinitriles **XIa/XIb** did not change the transformation pathway in homogeneous acid system. By contrast, in the presence of H-β-zeolite as catalyst, the transformation direction depends on the functional group nature. This is consistent with our previous assumption [12] that the intermediate species in the cyclization of 6,7-epoxy derivatives **Xa/Xb** is cation **A** (Scheme 5) which cannot be formed from **XIa/XIb**.

Compounds **IVa**, **IVb**, **V**, **XIa**, **XIb**, **XIIa**, **XIIb**, **XIII**, **XIVa**, **XIVb**, **XVIa**, and **XVIb** were not described previously; their structure was determined on the basis of the ^{1}H ad ^{13}C NMR and high-resolution mass spectra. Comparison of the chemical shifts of carbon nuclei in the ^{13}C NMR spectra of compounds **XIVa** and **XIVb** with those reported for structurally related *trans* and *cis* isomers **XIXa** and **XIXb** [13] allowed us to assign *trans* configuration to isomer **XIVa**, and *cis*, to **XIVb**.



XIXa



XIXb

R = CH_2=CH, $HOCH_2$.

The results of our study showed that reactions of terpenoid epoxy aldehydes with malononitrile in the presence of basic Cs-exchanged β-zeolite give mainly the corresponding epoxy dinitriles in fairly good yields. Epoxy dinitriles **XIa/XIb** in acid medium undergo various transformations whose direction is determined by the nature of acid catalyst. In the system dioxane–water–sulfuric acid, substituted tetrahydrofuran derivatives **XIVa/XIVb** are formed, while in the presence of acid H-β-zeolite compounds **XIa/XIb** are converted into acyclic polyenes **XVIa/ XVIb**.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer at 400.13 Hz for ^{1}H and 100.61 MHz for ^{13}C using CCl_4–$CDCl_3$ (1:1, by volume) as solvent; the chemical shifts were measured relative to the solvent signals ($CHCl_3$, δ 7.24 ppm; $CDCl_3$, δ_C 76.90 ppm). Signals were assigned by analysis of coupling constants in the ^{1}H–^{1}H double resonance spectra, ^{13}C NMR spectra recorded with selective decoupling from protons, off-resonance spectra, two-dimensional ^{13}C–^{1}H correlation spectra (CH-COSY, direct C–H coupling constants, $^1J_{CH}$ = 135 Hz), and one-dimensional ^{13}C–^{1}H correlation spectra (LRJMD, $^{2,3}J_{CH}$ = 10 Hz). The atom numbering in the NMR spectra given below corresponds to the atom numbering in the schemes.

The initial compounds and reaction products were analyzed by GLC on a Biokhrom-1 chromatograph using the following columns: (a) SE-54 quartz capillary column, 13000×0.22 mm, and (b) VS-30 (analog of SE-30) quartz capillary column, 20000×0.27 mm; flame ionization detector, carrier gas helium. The product mixtures were separated by column chromatography on silica gel (ChFSR, 100–160 μm). The elemental compositions were determined from the

high-resolution mass spectra which were recorded on a Finnigan MAT-8200 instrument.

Commercial technical-grade citral was used (*E*/*Z* isomer ratio 1.5:1, according to the ^{1}H NMR data). The synthesis and properties of basic Cs-exchanged β-zeolite were described in [2]; wide-pore acid β-zeolite (H form, manufactured by *Tseosit* Research Center, Novosibirsk, Russia) had a SiO_2/Al_2O_3 ratio of 22.4, pore diameter 0.75–0.80 nm, and the following oxide weight percentage: Na_2O, 0.1; Al_2O_3, 4.50; SiO_2, 59.20; Fe_2O_3, 0.08%. The catalysts were calcined for 3 h at 500°C just before use. Diethyl ether and methylene chloride were dried by passing through a column charged with calcined aluminum oxide.

Compounds **IIIa/IIIb** were synthesized according to the procedure described in [11] by treatment of citral with hydrogen peroxide under conditions of phase-transfer catalysis. From 3 g of technical-grade citral we obtained 2.35 g of a mixture of isomeric 2,3-epoxy derivatives **IIIa** and **IIIb** with an *E*/*Z* ratio of 1.2:1 (according to the ^{1}H NMR data). Compounds **Xa/Xb** were synthesized according to [10] by reaction of citral with peroxyacetic acid. From 3 g of technical-grade citral we obtained 2.8 g of a crude product from which 1.1 g of isomer mixture **Xa/Xb** ($E:Z \approx 1.2:1$, ^{1}H NMR data) was isolated.

Reaction of 2,3-epoxy citrals IIIa/IIIb with malononitrile over Csβ-zeolite. A solution of 0.15 g of malononitrile in 3 ml of diethyl ether was added to a suspension of 0.05 g of Csβ in 5 ml of diethyl ether, a solution of 0.200 g of isomer mixture **IIIa/IIIb** in 2 ml of diethyl ether was then added, and the mixture was stirred for 2 h at room temperature. The catalyst was filtered off and washed with ethyl acetate. After removal of the solvent, the residue was subjected by column chromatography on silica gel using hexane–diethyl ether as eluent (gradient elution, 5 to 100% of diethyl ether) to isolate 0.089 g of isomeric 2-[3-methyl-3-(4-methylpent-3-en-1-yl)oxiran-2-ylmethylidene]-malononitriles **IVa/IVb** (~1.2:1, ^{1}H NMR), and 0.039 g of a mixture of compounds **IVa**, **IVb**, and 2-(3-isopropenyl-6-methyl-7-oxabicyclo[4.1.0]hept-2-yl)-malononitrile (**V**) at a ratio of ~0.4:1.0:0.3 (^{1}H NMR). Overall yield 50%; calculated yields of **IVa/IVb** and **V** 47 and 3%, respectively.

The NMR spectra of compounds **IVa/IVb** were recorded from their mixtures containing one or another isomer as the major component.

(*E*)-2-[3-Methyl-3-(4-methylpent-3-en-1-yl)oxiran-2-ylmethylidene]malononitrile (IVa). ^{1}H NMR spectrum, δ, ppm: 1.35 s ($C^{11}H_3$), 1.58 br.s ($C^{10}H_3$), 1.67 m (C^9H_3), 1.57 m and 1.78 m (2H, 5-H), 2.09 m (2H, 6-H), 3.62 d (3-H, $J_{3,2}$ = 8 Hz), 5.04 t.q.q (7-H, $J_{7,6}$ 7, $J_{7,9}$ = 1.2, $J_{7,10}$ = 1.2 Hz), 7.06 d (2-H, $J_{2,3}$ = 8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 91.33 s (C^1), 163.76 d (C^2), 59.60 d (C^3), 66.86 s (C^4), 38.03 t (C^5), 23.29 t (C^6), 122.10 d (C^7), 132.96 s (C^8), 25.44 q (C^9), 17.47 q (C^{10}), 17.39 q (C^{11}), 111.38 s (C^{12}), 109.89 s (C^{13}). Found: *M* 173.07226. $C_{10}H_9N_2O$ ($M - C_3H_7$). Calculated: *M* 173.07148.

(*Z*)-2-[3-Methyl-3-(4-methylpent-3-en-1-yl)oxiran-2-ylmethylidene]malononitrile (IVb). ^{1}H NMR spectrum, δ, ppm: 1.44 s ($C^{11}H_3$), 1.59 br.s ($C^{10}H_3$), 1.67 m (C^9H_3), 1.43 m and 1.76 m (2H, 5-H), 2.06 m and 2.16 m (2H, 6-H), 3.58 d (3-H, $J_{3,2}$ = 8 Hz), 4.99 t.q.q (7-H, $J_{7,6}$ = 7, $J_{7,9}$ = 1.2, $J_{7,10}$ = 1.2 Hz), 7.04 d (2-H, $J_{2,3}$ = 8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 90.72 s (C^1), 163.76 d (C^2), 60.48 d (C^3), 67.05 s (C^4), 33.63 t (C^5), 23.80 t (C^6), 121.95 d (C^7), 133.55 s (C^8), 25.54 q (C^9), 17.39 q (C^{10}), 21.84 q (C^{11}), 111.38 s (C^{12}), 109.85 s (C^{13}).

2-(3-Isopropenyl-6-methyl-7-oxabicyclo[4.1.0]-hept-2-yl)malononitrile (V). The NMR spectra of **V** were obtained from the spectra of a mixture of compounds **IVa**, **IVb**, and **V** at a ratio of ~0.4:1.0:0.3. ^{1}H NMR spectrum, δ, ppm: 1.39 s ($C^{11}H_3$), 1.73 br.s ($C^{10}H_3$), 2.50 d.d.d.m (7-H, $J_{7,6}$ = 11, $J_{7,2}$ = 5, $J_{7,6'}$ = 3.5 Hz), 2.82 d.d.d (2-H, $J_{2,1}$ = 5, $J_{2,7}$ = 5, $J_{2,3}$ = 2 Hz), 3.20 d (3-H, $J_{3,2}$ = 2 Hz), 3.94 d (1-H, $J_{1,2}$ = 5 Hz), 4.71 m and 5.10 m (2H, 9-H). ^{13}C NMR spectrum, δ_C, ppm: 21.54 d (C^1), 39.61 d (C^2), 59.16 d (C^3), 58.54 s (C^4), 26.12 t (C^5), 20.12 t (C^6), 37.83 d (C^7), 144.00 s (C^8), 113.46 q (C^9), 22.82 q (C^{10}), 23.46 q (C^{11}), 112.10 s and 112.45 s (C^{12}, C^{13}).

Reaction of 6,7-epoxy citrals Xa/Xb with malononitrile over Csβ-zeolite. A solution of 1.0 g of malononitrile in 20 ml of diethyl ether was added to a suspension of 0.15 g of Csβ in 10 ml of diethyl ether, a solution of 0.978 g of isomer mixture **Xa/Xb** in 10 ml of diethyl was then added, and the mixture was stirred for 4 h at room temperature. The catalyst was filtered off and washed with ethyl acetate, and the solvent was removed from the filtrate to leave 1.7 g of a product mixture which was subjected to column chromatography on silica gel (gradient elution with hexane–diethyl ether, 5 to 100% of the latter). We isolated 0.750 g (62%) of 2-[5-(3,3-dimethyloxiran-2-yl)-3-methylpent-2-en-1-ylidene]malononitriles **XIa/XIb** (~1.7:1, ^{1}H NMR), 0.024 g (2%) of 5-(3,3-dimethyloxiran-2-yl)-3-methylpent-2-enoic acids **XIIa/XIIb**

(~1.0:0.6, ^{1}H NMR), and 0.033 g (3%) of 7-(1-hydroxy-1-methylethyl)-4-methyl-6,7-dihydrooxepin-2(5*H*)-one (**XIII**).

The NMR spectra of compounds **XIa** and **XIb** were recorded from their mixture at a ratio of ~1.0:0.5.

(*E*)-2-[5-(3,3-Dimethyloxiran-2-yl)-3-methylpent-2-en-1-ylidene]malononitrile (XIa). ^{1}H NMR spectrum, δ, ppm: 1.22 s and 1.26 s (C^9H_3, $C^{10}H_3$), 1.65 m and 1.76 m (2H, 6-H), 2.00 d ($C^{11}H_3$, $J_{11,3}$ = 1.2 Hz), 2.35–2.52 m (2H, 5-H), 2.66 d.d (7-H, $J_{7,6}$ = 7.5, $J_{7,6'}$ = 5 Hz), 6.46 d.m (3-H, $J_{3,2}$ = 12 Hz), 7.74 d (2-H, $J_{2,3}$ = 12 Hz). ^{13}C NMR spectrum, δ_C, ppm: 81.26 s (C^1), 155.90 d (C^2), 121.29 d (C^3), 163.84 s (C^4), 37.60 t (C^5), 26.74 t (C^6), 63.02 d (C^7), 58.33 s (C^8), 24.23 q and 18.41 q (C^9, C^{10}), 18.55 q (C^{11}), 113.62 s (C^{12}), 111.44 s (C^{13}).

(*Z*)-2-[5-(3,3-Dimethyloxiran-2-yl)-3-methylpent-2-en-1-ylidene]malononitrile (XIb). ^{1}H NMR spectrum, δ, ppm: 1.22 s and 1.26 s (C^9H_3, $C^{10}H_3$), 1.57 m and 1.74 m (2H, 6-H), 2.05 d ($C^{11}H_3$, $J_{11,3}$ = 1.2 Hz), 2.35–2.52 m (2H, 5-H), 2.64 d.d (7-H, $J_{7,6}$ = 8, $J_{7,6'}$ = 4.5 Hz), 6.46 d.m (3-H, $J_{3,2}$ = 12 Hz), 7.77 d (2-H, $J_{2,3}$ = 12 Hz). ^{13}C NMR spectrum, δ_C, ppm: 81.26 s (C^1), 155.27 d (C^2), 122.28 d (C^3), 163.88 s (C^4), 30.56 t (C^5), 27.39 t (C^6), 62.77 d (C^7), 58.56 s (C^8), 24.38 q and 18.43 q (C^9, C^{10}), 25.11 q (C^{11}), 113.62 s (C^{12}), 111.44 s (C^{13}).

The NMR spectra of compounds **XIIa** and **XIIb** were recorded from their mixture at a ratio of ~1.0:0.6.

(*E*)-5-(3,3-Dimethyloxiran-2-yl)-3-methylpent-2-enoic acid (XIIa). IR spectrum, ν, cm^{-1}: 1700 (C=O), 3452 (OH). ^{1}H NMR spectrum, δ, ppm: 1.23 s and 1.27 s (C^8H_3, C^9H_3), 1.58–1.82 m (2H, 5-H), 2.15 d ($C^{10}H_3$, $J_{10,2}$ = 1.2 Hz), 2.25 m and 2.33 m (2H, 4-H), 2.68 d.d (6-H, $J_{6,5}$ = 7, $J_{6,5'}$ = 6 Hz), 5.69 m (2-H). ^{13}C NMR spectrum, δ_C, ppm: 171.52 s (C^1), 115.49 d (C^2), 161.47 s (C^3), 37.69 t (C^4), 26.75 t (C^5), 63.37 d (C^6), 58.50 s (C^7), 24.59 q and 18.55 q (C^8, C^9), 18.95 q (C^{10}). Found: *M* 184.10980. $C_{10}H_{16}O_3$. Calculated: *M* 184.10994.

(*Z*)-5-(3,3-Dimethyloxiran-2-yl)-3-methylpent-2-enoic acid (XIIb). ^{1}H NMR spectrum, δ, ppm: 1.23 s and 1.26 s (C^8H_3, C^9H_3), 1.58–1.82 m (2H, 5-H), 1.91 d ($C^{10}H_3$, $J_{10,2}$ = 1.2 Hz), 2.64 d.d.d (4-H, $J_{4,4'}$ = 12, $J_{4,5}$ = 9, $J_{4,5'}$ = 6 Hz), 2.75 t (6-H, $J_{6,5}$ = 6.5 Hz), 2.82 d.d.d (4'-H, J = 12, $J_{4',5'}$ = 9, $J_{4',5}$ = 6 Hz), 5.69 m (2-H). ^{13}C NMR spectrum, δ_C, ppm: 171.11 s (C^1), 116.16 d (C^2), 162.12 s (C^3), 30.09 t (C^4), 27.43 t (C^5), 63.73 d (C^6), 58.50 s (C^7), 24.63 q and 18.43 q (C^8, C^9), 25.38 q (C^{10}).

7-(1-Hydroxy-1-methylethyl)-4-methyl-6,7-dihydrooxepin-2(5*H*)-one (XIII). ^{1}H NMR spectrum, δ, ppm: 1.21 s and 1.23 s (C^9H_3, $C^{10}H_3$), 1.88 d.d.d.d (6-H, $J_{6,6'}$ = 14.5, $J_{6,7}$ = 9, $J_{6,5}$ = 9, $J_{6,5'}$ = 6 Hz), 1.91 d ($C^{11}H_3$, $J_{11,3}$ = 1.2 Hz), 2.07 d.d.d.d (6'-H, J = 14.5, $J_{6',5}$ = 6, $J_{6',5'}$ = 5.5, $J_{6',7}$ = 2.2 Hz), 2.27 d.d.d.d (5-H, $J_{5,5'}$ = 18, $J_{5,6}$ = 9, $J_{5,6'}$ = 6, $J_{5,3}$ = 1.2 Hz), 2.46 d.d.d.d (5'-H, J = 18, $J_{5',6}$ = 6, $J_{5',6'}$ = 5.5, $J_{5',3}$ = 1.2 Hz), 3.99 d.d (7-H, $J_{7,6}$ = 9, $J_{7,6'}$ = 2.2 Hz), 5.81 m (3-H, $J_{3,11}$ = $J_{3,5}$ = $J_{3,5'}$ = 1.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 168.02 s (C^2), 118.15 d (C^3), 154.69 t (C^4), 33.40 t (C^5), 27.10 t (C^6), 84.25 d (C^7), 71.48 s (C^8), 24.56 q and 24.95 q (C^9, C^{10}), 25.96 q (C^{11}). Found: *M* 184.11000. $C_{10}H_{16}O_3$. Calculated: *M* 184.10994.

Transformation of 6,7-epoxy citrals Xa/Xb over Csβ-zeolite. A solution of 0.070 g of isomer mixture **Xa/Xb** in 2 ml of diethyl ether was added to 0.05 g of Csβ, the solvent was distilled off on a rotary evaporator, and the residue was kept for 8 days at room temperature. It was then extracted with diethyl ether, the catalyst was filtered off and washed with diethyl ether, and the solvent was removed to obtain 0.052 g of a mixture containing initial compounds **Xa/Xb** (calculated conversion 36%) and lactone **XIII** (26%, calculated on the reacted initial compound) at a ratio of 7:1 (^{1}H NMR data).

Transformation of isomeric epoxy dinitriles XIa/XIb in the system dioxane–water–H_2SO_4. Isomer mixture **XIa/XIb** (~1.7:1), 0.100 g, was added to 1.5 ml of a dioxane–water–sulfuric acid mixture at a volume ratio of 40:6:1. After 5 min, the mixture was treated with a saturated solution of sodium carbonate and extracted with diethyl ether. Removal of the solvent from the extract left 0.08 g of a crude product containing compounds **XIVa** and **XIVb** at a ratio of ~1:1.5 (GLC). By column chromatography on silica gel (gradient elution with hexane–diethyl ether, 0.5 to 30% of the latter) we isolated 0.02 g (18%) of a mixture of **XIVa** and **XIVb** at a ratio of ~1:0.6 (GLC and ^{1}H NMR data).

The NMR spectra of compounds **XIVa** and **XIVb** were recorded from their mixture at a ratio of 1.0:0.6.

(*E*)-2-{2-[5-(1-Hydroxy-1-methylethyl)-2-methyltetrahydrofuran-2-yl]ethylidene}malononitrile (XIVa). ^{1}H NMR spectrum, δ, ppm: 1.11 s and 1.21 s (C^9H_3, $C^{10}H_3$), 1.25 s ($C^{11}H_3$), 1.75–1.98 m (4H, 5-H, 6-H), 2.71–2.82 m (2H, 3-H), 3.77 d.d (7-H, $J_{7,6}$ = 9, $J_{7,6'}$ = 6 Hz), 7.43 t (2-H, $J_{2,3}$ = 8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 91.40 s (C^1), 166.34 d (C^2), 44.00 t (C^3), 82.18 s (C^4), 38.08 t (C^5), 26.04 t (C^6), 86.52 d

(C^7), 70.55 s (C^8), 24.12 q and 27.26 q (C^9, C^{10}), 27.00 q (C^{11}), 111.94 s (C^{12}), 110.56 s (C^{13}).

(*Z*)-2-{2-[5-(1-Hydroxy-1-methylethyl)-2-methyltetrahydrofuran-2-yl]ethylidene}malononitrile (XIVb). ^{1}H NMR spectrum, δ, ppm: 1.12 s and 1.22 s (C^9H_3, $C^{10}H_3$), 1.24 s ($C^{11}H_3$), 1.75–1.98 m (4H, 5-H, 6-H), 2.77 d (2H, 3-H, $J_{3,2}$ = 8 Hz), 3.81 d.d (7-H, $J_{7,6}$ = 8, $J_{7,6'}$ = 7 Hz), 7.52 t (2-H, $J_{2,3}$ = 8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 91.14 s (C^1), 166.88 d (C^2), 44.53 t (C^3), 82.00 s (C^4), 37.79 t (C^5), 26.04 t (C^6), 85.57 d (C^7), 71.08 s (C^8), 24.84 q and 27.04 q (C^9, C^{10}), 26.13 q (C^{11}), 111.94 s (C^{12}), 110.70 s (C^{13}).

Transformation of isomeric epoxy dinitriles XIa/XIb over acid β-zeolite. Isomer mixture **XIa/XIb** (~1.7:1), 0.230 g, was added to a suspension of 0.3 g of calcined β-zeolite (H form) in 4 ml of anhydrous methylene chloride. The mixture was stirred for 30 min (the catalyst turned orange–brown) and filtered, the catalyst was washed with diethyl ether, the solvent was removed from the filtrate, and the residue (0.17 g) was subjected to column chromatography on silica gel (gradient elution with hexane–diethyl ether, 0.5 to 30% of the latter). We isolated 0.077 g of unreacted initial compounds (conversion 67%, *E*/*Z* ratio ~7:1, according to the ^{1}H NMR data), 0.005 g of compound **XVIa**, and 0.021 g of isomer **XVIb**; overall yield of **XVIa** and **XVIb** 17% (calculated on the reacted initial compounds).

(*E*)-2-(6-Hydroxy-3,7-dimethylocta-2,7-dien-1-ylidene)malononitrile (XVIa). ^{1}H NMR spectrum, δ, ppm: 1.64–1.73 m (2H, 6-H), 1.72 br.s ($C^{10}H_3$), 2.04 d ($C^{11}H_3$, $J_{11,3}$ = 1.2 Hz), 2.28–2.46 m (2H, 5-H), 4.03 m (7-H), 4.85 d.q.d (9-H, $J_{9,9'}$ = 2, $J_{9,10}$ = 1.5, $J_{9,7}$ = 0.5 Hz), 4.94 d.d.q (9'-H, J = 2, $J_{9',7}$ = 1, $J_{9',10}$ = 0.5 Hz), 6.48 d.q.m (3-H, $J_{3,2}$ = 12, $J_{3,11}$ = 1.2 Hz), 7.68 d (2-H, J = 12 Hz). ^{13}C NMR spectrum, δ_C, ppm: 82.32 s (C^1), 155.05 d (C^2), 121.53 d (C^3), 163.61 s (C^4), 37.07 t (C^5), 32.51 t (C^6), 74.80 d (C^7), 146.88 s (C^8), 111.62 t (C^9), 17.80 q (C^{10}), 18.80 q (C^{11}), 113.43 s (C^{12}), 111.28 s (C^{13}).

(*Z*)-2-(6-Hydroxy-3,7-dimethylocta-2,7-dien-1-ylidene)malononitrile (XVIb). ^{1}H NMR spectrum, δ, ppm: 1.65 m (2H, 6-H), 1.71 br.s ($C^{10}H_3$), 2.08 d ($C^{11}H_3$, $J_{11,3}$ = 1.2 Hz), 2.33–2.59 m (2H, 5-H), 3.93 m (7-H), 4.86 d.q (9-H, $J_{9,9'}$ = 2, $J_{9,10}$ = 1.2 Hz), 4.95 d.d (9'-H, J = 2, $J_{9',7}$ = 1 Hz), 6.48 d.m (3-H, $J_{3,2}$ = 12 Hz), 7.81 d (2-H, J = 12 Hz). ^{13}C NMR spectrum, δ_C, ppm: 82.12 s (C^1), 155.13 d (C^2), 122.67 d (C^3), 163.40 s (C^4), 29.83 t (C^5), 33.07 t (C^6), 74.06 d (C^7), 147.00 s (C^8), 111.54 t (C^9), 17.94 q (C^{10}), 25.32 q (C^{11}), 113.53 s (C^{12}), 111.32 s (C^{13}).

REFERENCES

1. Sheldon, R.A. and Downing, R.S., *Appl. Catal. A: General*, 1999, vol. 189, p. 163.
2. Corma, A. and Ibora, S., *Fine Chemicals through Heterogeneous Catalysis*, Sheldon, R.A. and van Bekkum, H., Eds., Weinheim: Wiley, 2001, p. 309.
3. Volcho, K.P., Kurbakova, S.Yu., Korchagina, D.V., Suslov, E.V., Salakhutdinov, N.F., Toktarev, A.V., Echevskii, G.V., and Barkhash, V.A., *J. Mol. Catal. A: Chem.*, 2003, vol. 195, p. 263.
4. Volcho, K.P., Suslov, E.V., Kurbakova, S.Yu., Korchagina, D.V., Salakhutdinov, N.F., and Barkhash, V.A., *Russ. J. Org. Chem.*, 2004, vol. 40, p. 659.
5. Kryshtal', G.V. and Serebryakov, E.P., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1995, p. 1867.
6. Nigmatov, A.G. and Serebryakov, E.P., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, p. 605.
7. Kotera, M., Ishii, K., Tamura, O., and Sakamoto, M., *J. Chem. Soc., Perkin Trans. 1*, 1998, p. 313.
8. Luzina, O.A., Korchagina, D.V., Salakhutdinov, N.F., and Barkhash, V.A., *Zh. Org. Khim.*, 1994, vol. 30, p. 784.
9. Smit, V.A. and Kucherov, V.F., *Usp. Khim.*, 1959, vol. 28, p. 272.
10. Yarovaya, O.I., Korchagina, D.V., Salomatina, O.V., Polovinka, M.P., and Barkhash, V.A., *Mendeleev Commun.*, 2003, no. 1, p. 28.
11. Yarovaya, O.I., Korchagina, D.V., Salomatina, O.V., Polovinka, M.P., and Barkhash, V.A., *Russ. J. Org. Chem.*, 2003, vol. 39, p. 985.
12. Yarovaya, O.I., Salomatina, O.V., Korchagina, D.V., Polovinka, M.P., and Barkhash, V.A., *Russ. J. Org. Chem.*, 2002, vol. 38, p. 1594.
13. Francisco, C.G., Freire, R., Hernandez, R., Salazar, J.A., Suarez, E., and Cortes, M., *Org. Magn. Reson.*, 1984, vol. 22, p. 34.