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Conversions of Allyl Ethers in a Superbasic Medium

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Abstract—Conversions of alkyl allyl and terpenoid allyl ethers in a superbasic medium (dimethyl sulfoxide–potassium hydroxide) are studied. The ethers with an unbranched alkyl substituent isomerize into propenyl ethers, the ethers with a branched unsaturated substituent decompose to give a hydrocarbon, and diallyl ethers isomerize into allyl vinyl ethers whose Claisen rearrangement gives rise to aldehydes.

Earlier we showed that certain allyl ethers derived from terpene alcohols undergo Wittig rearrangement under the action of butyllithium [1]. According to present views, this rearrangement occurs as a 2,3-alkyl shift in the anion formed by deprotonation of the ethers, via a five-membered transition state [2].

Thus obtained secondary terpenoid alcohols have a pleasant flowery wood odor and can be used as fragnances. This prompted us to study the Wittig rearrangement in more “practicable” conditions, as well as to bring into this rearrangement a wider range of ethers ROCHCH=CH_2, where R is aliphatic and mono- and bicyclic terpene radicals.

Wittig rearrangement is catalyzed by strong bases which induce carbanion formation [2]. We applied as a superbasic medium the system KOH–DMSO [3]. This system is widely used in organic synthesis. The objects for study were structurally diverse ethers, primarily terpenoid: allyloxyoctane (**I**), allyloxydecane (**II**), 10-allyloxymethyl-α-pinene (allyl ether of nopol) (**III**), 6-allyloxymethyl-1,8-*p*-mentadiene (allyl ether of 6-hydroxymethyllimonene] (**IV**), 6-allyloxymethyl-2,8-*p*-mentadiene (allyl ether of 6-hydroxymethylisolimonene) (**V**), 4-allyloxymethyl-2-carene (allyl ether of waltherol) (**VI**), 2-allyloxymethyl-3-carene (allyl ether of isowaltherol) (**VII**), 1-allyloxy-3,7-dimethyl-2,6-octadiene (allyl ether of geraniol) (**VIII**), and 8-allyloxymethylcamphene (**IX**).

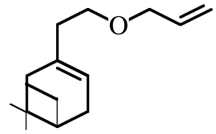
The reaction was performed at a 1 : 5 : 30 substrate–KOH–DMSO ratio at 120°C for 4 h. The reaction product after workup (see Experimental) was analyzed by GLC.

Depending on the nature of the starting ether, three types of compounds were formed: hydrocarbons, propenyl ethers, and aldehydes. Contrary to expectations, secondary alcohols were not found among the reaction products. Thus, we can state that with such a superbase as KOH–DMSO no Wittig rearrangement occurs. A possible reason is that, unlike lithium (alkyllithiums are typical catalysts of Wittig rearrangement), the potassium ion is rather large and cannot be incorporated into a cyclic transition state [4].

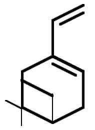
Allyl ethers **I** and **II** quantitatively converted into propenyl ethers **X** and **XI**, respectively. Such a base-induced isomerization has been reported [5]. It is characteristic of ethers with a linear alkyl group whose free rotation about C–C bonds prevents molecular fragments from approaching each other at a distance necessary to form the transition state for the sigmatropic shift; the reaction occurs through an allyl anion.

$$CH_3(CH_2)_nCH_2OCH_2CH{=}CH_2$$
$$\rightarrow CH_3(CH_2)_nCH_2OCH{=}CHCH_3,$$
$$n = 6\ (\mathbf{X}),\ 8\ (\mathbf{XI}).$$

Ether **III** converted into 6,6-dimethyl-2-vinylbicyclo[3.1.1]hept-2-ene (**XII**) (10-methylene-α-pinene, “nopadiene”). The formation of the same hydrocarbon by the decomposition of 6,6-dimethyl-2-(2-methoxyethyl)bicyclo[3.1.1]hept-2-ene (**XIII**) (methyl ether of nopol) under the action of a mixed catalyst, lithium diisopropylamine–potassium *tert*-butylate has been reported [6].

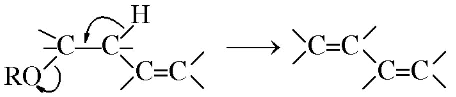


III



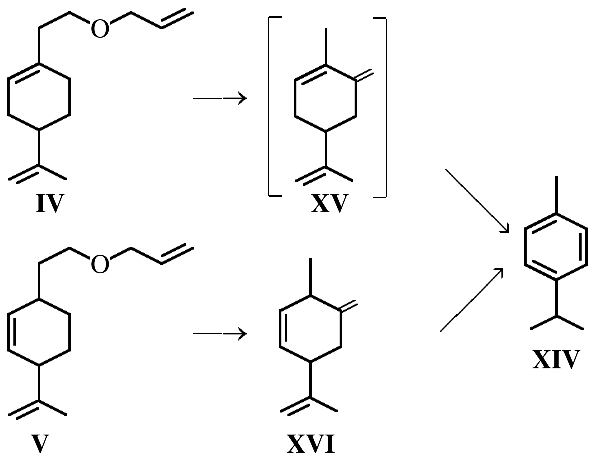
XII

The authors explained the decomposition of ether **XIII** and other homoallyl (i.e. γ,δ-unsaturated) ethers by the mobility of allyl proton; as a result, 1,2-elimination by the *E*1cb-like mechanism takes place, yielding a 1,3-diene system. It was also noted that an additional alkyl substituent in the β position appreciably decelerates the reaction and decreases the yield of the diene.



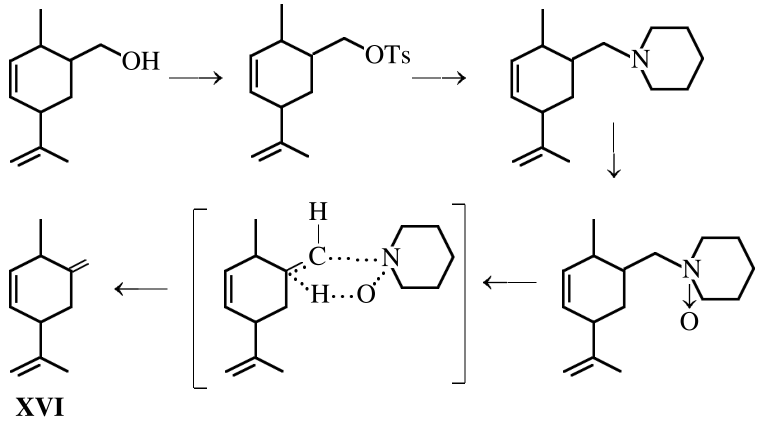
Under our conditions, alcohol elimination from ethers **III**–**VII** occurred smoothly and in high yields.

Conversions of ethers **IV** and **V** in KOH–DMSO gave one and the same product, 4-isopropyl-1,2-dimethylbenzene (**XIV**). It is reasonable to suggest that ether **IV** which is simultaneously an allyl and a homoallyl ether undergoes 1,2 elimination, and triene **XV** that forms isomerizes into a stable aromatic structure. Such conversions under the action of *t*-BuOK are known [7].



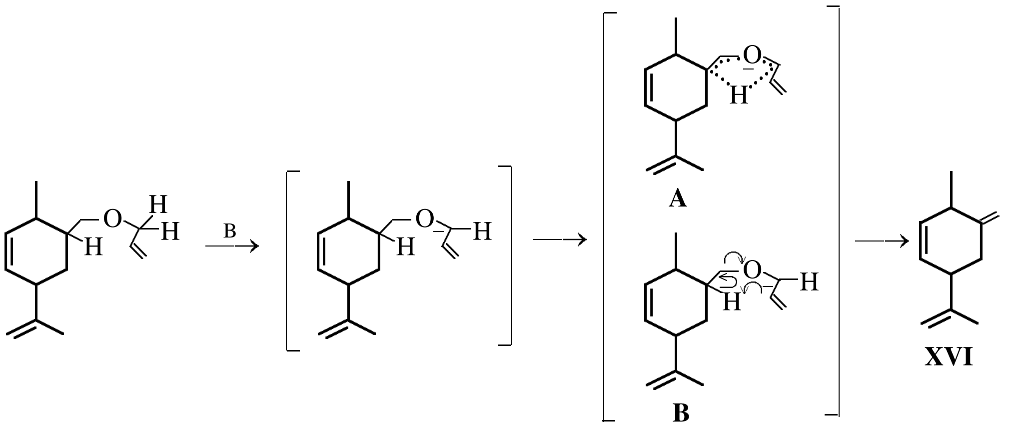
However, this mechanism fails to explain the formation of hydrocarbon **XIV** from ether **V** (δ,ε-unsaturated). Obviously, the isomerization leading to a vinyl ether, like with ethers **I** and **II**, also does not occur.

To find out the nature of the primary product of the conversion of ether **V**, we performed this reaction at a lower temperature. After 80°C at 12 h, the reaction mixture, according to GCL data, contained 85% of unreacted ether and 15% of hydrocarbons. The hydrocarbon fraction comprised four components, one prevailing (~60%); among the other three we identified **XIV** (26%) and **XV** (8%). Gas-chromatographic analysis of this mixture with added authentic sample obtained by independent synthesis showed that the prevailing hydrocarbon component was 6-methylene-*p*-menta-2,8-diene (**XVI**) whose independent synthesis was performed from 6-(hydroxymethyl)isolimonene.



Formally, this hydrocarbon is formed by 1,2 elimination in the reaction of ether **V** with the base, but the E1cb mechanism is unlikely because of the absence of a sufficienly acidic proton in the β position.

From out viewpoint, the elimination in the case of ether **V** may occur in the following way. The base acts on the mobile proton of the allyl substituent to give the E1cb transition state. However, because of the specific molecular geometry of ether **V**, this transition state, rather than transforming into the allyl anion, transforms into cyclic transition state **A**.



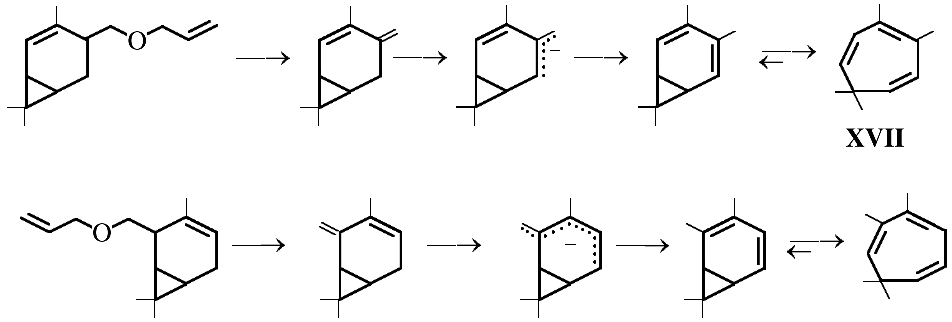
A

B

XVI

This five-membered transition state (including a negatively charged carbon atom) is quasiaromatic. Thus, a symmetry-allowed suprafacial 1,4-hydrogen shift takes place [8], leading to elimination of allyl alcohol and formation of hydrocarbon **XVI** and then aromatic structure **XV**. In terms of the "push–pull" mechanism, we can suggest transition state **B**.

With ethers **VI** and **VII** which are simultaneously allyl and homoallyl, both mechanisms are possible: E1cb-like and sigmatropic, and they both should lead to one and the same compound. The structures of the products formed from ethers **VI** and **VII**, substituted cycloheptatrienes **XVII** and **XVIII**, respectively, suggests initial formation of caradienes **XIX** and **XX** with a terminal double bond. Their base-induced isomerization into 2,4-caradienes [9] and valence tautomerization of the latter, strongly shifted to the monocycle [10], result in selective formation of trienes **XVII** and **XVIII**.



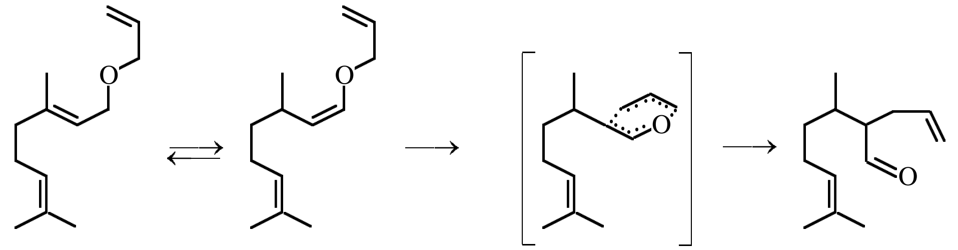
XVII

VII XX XVIII

Ether **VIII** and **IX** in the superbasic medium convert into γ,δ-unsaturated aldehydes, implying the possibility of Claisen rearrangement. For this rearrangement to occur, allyl allyl ethers should first isomerize into allyl vinyl. The possibility of such a transformation in the reaction studied was demonstrated by the example of ethers **I** and **II**.

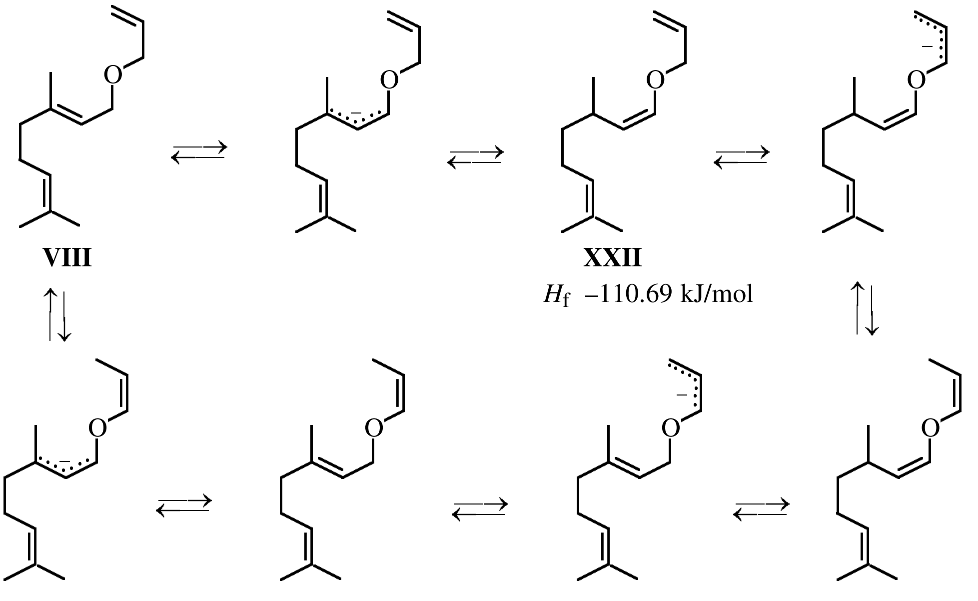
Ethers **VIII** and **IX** may formally give two allyl vinyl ethers, which should result in formation of two different aldehydes in each case. However, experimentally, this proved not the case. The transformation product of ether **VIII** was identified as 2-allyl-3,7-dimethyloctanal (**XXI**).

The structure of this aldehyde points to the fact that only one of the possible isomers, ether **XXII**, formed by double-bond shift in the geranyl substituent, undergoes rearrangement in this case. Under the reaction conditions, this ether is in dynamic equilibrium with other ethers, including ether **XXIII** formed by double-bond shift in the allyl substituent. Semiempi-



VIII **XXII** **XXI**

rical MNDO–PM3 calculations with gradient geometry optimization [11] show that ether **XXII** is much less stable than ether **XXIII** and, correspondingly, it is much more susceptible to thermal rearrangement. It should be noted that the geometry of the allyloxyvinyl fragment of ether **XXII** is close to that calculated at the RHF/6-31G* level [12], and, therewith, the distance between the terminal atoms of the double bonds (which should approach each other to form the transition state) in ether **XXII** is shorter than in unsubstituted allyl vinyl ether (4.79 and 5.28 Å, respectively). Thus, the selectivity of the reaction is governed by the thermodynamic factor.



VIII

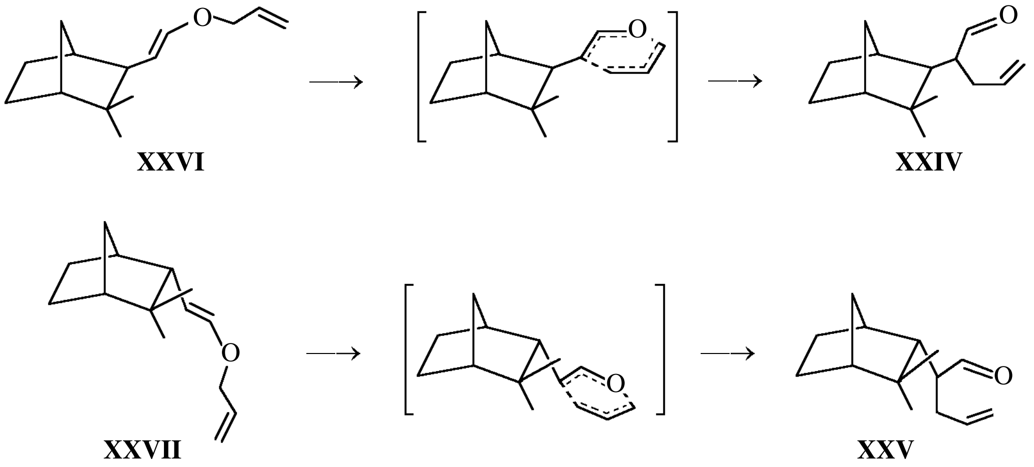
XXII
H_f –110.69 kJ/mol

XXIII
H_f –156.12 kJ/mol

The transformation product of ether **IX**, according to GLC data, was a mixture of two components (9 : 1). By ^{1}H NMR spectroscopy we identified them as *exo*- and *endo*-2-(3,3-dimethylbicyclo[2.2.1]hept-2-yl)pent-4-enals (**XXIV, XXV**). The *exo* isomer is prevailing, which was established by the chemical shift and multiplicity of the signal of the proton on the C^2 atom of the isocamphane fragment: for aldehyde **XXIV** it is a doublet at δ 1.86 ppm (*J* 7.5 Hz), and for aldehyde **XXV**, a multiplet at δ 2.19–2.24 ppm.

As with ether **VIII**, only one of the two possible isomerization products of compound **IX**, specifically, that formed by double-bond shift in the 10-methylcamphene substituent, undergoes Claisen rearrangement. The specificity of the steric structure of this ether is that it exists as a mixture of stereoisomers **XXVI** and **XXVII**.

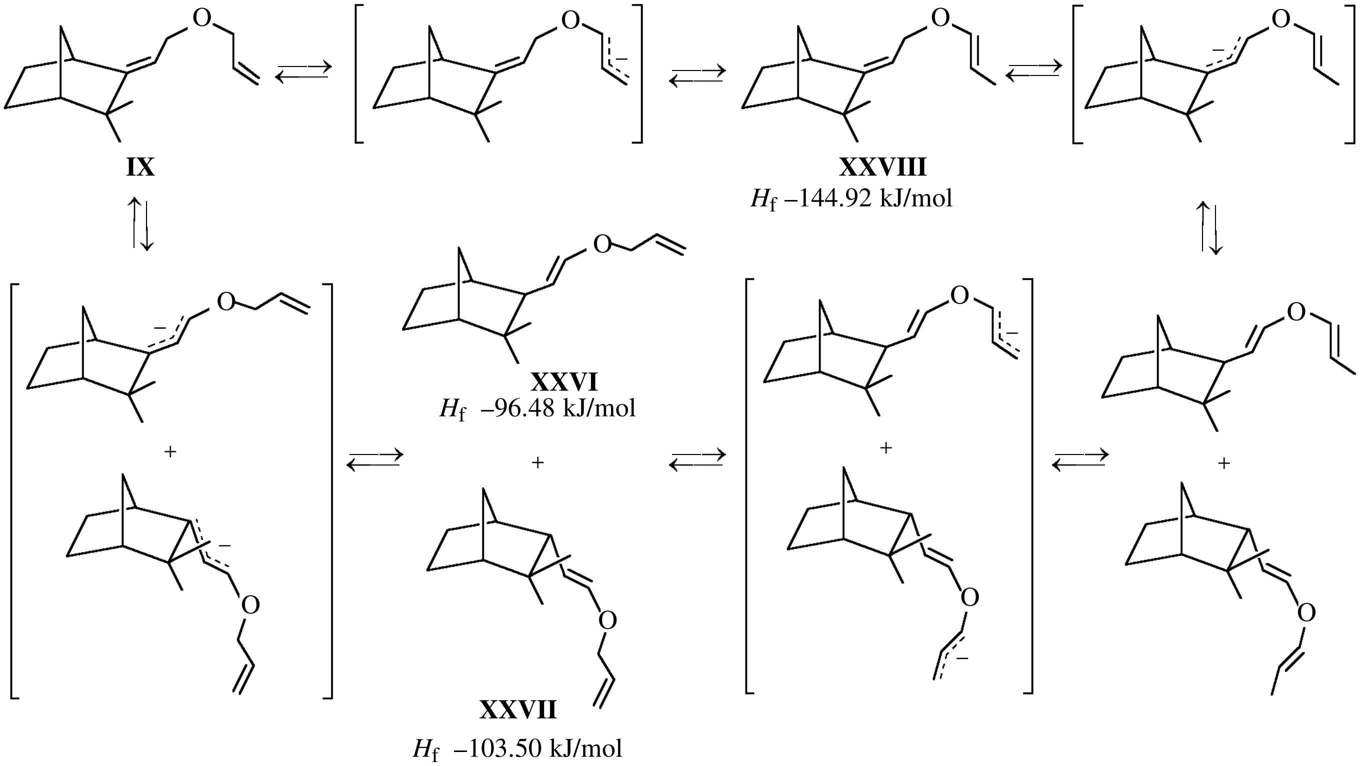
According to the calculation, these isomers both have higher heats of formation and, as a consequence,



XXVI **XXIV**

XXVII **XXV**

are more reactive than ether **XXVIII** formed by double-bond shift in the allyl substituent. Therewith, *exo* isomer **XXVI** is more reactive than *endo* isomer **XXVII**.



IX

XXVIII
H_f –144.92 kJ/mol

XXVI
H_f –96.48 kJ/mol

XXVII
H_f –103.50 kJ/mol

Moreover, the distances between the terminal atoms of the double bonds, which approach each other to form the transition state, in ethers **XXVI** and **XXVII** are 3.61 and 4.56 Å, respectively. Thus, with ether **XXVI**, Claisen rearrangement is preferred both energetically and structurally.

The resulting aldehydes have a pleasant odor: aldehyde **XXI**, woody flowery with sandal and patchouli accents and a mixture of aldehydes **XXIV** and **XXV**, woody flowery with cyclamen and patchouli accents, and can be used as fragnances.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Tesla BS-567A spectrometer in deuterochloroform against internal HMDS. Gas chromatography was performed on a Khrom-5 chromatograph with a flame ionization detector, column 2000 × 3 mm, carrier Chromaton N-AW-DMCS (fraction 0.125–0.160), liquid phase Reoplex-400, temperature programming from 100 to 180°C (4 deg/min), carrier gas nitrogen.

Allyl ethers were obtained by the procedure in [1].

Standard experimental procedure. Ground KOH, 0.5 mol, was vigorously stirred in 3 mol of DMSO at 100°C. After cooling to 70°C, allyl ether, 0.1 mol, was added dropwise. The mixture was then heated to 120°C, stirred at that temperature for 4 h, cooled, and diluted ten times with water. The organic layer was separated, and the reaction products were extracted from the aqueous layer with water with diethyl ether (2 × 50 ml). The organic layer was combined with the ether extracts, washed to neutral, and dried with $MgSO_4$. The solvent was removed, and the reaction product was distilled at reduced pressure.

The physicochemical and spectral properties of the products were consistent with published data: **XII** [6], **XIV** [13], **XVII** [9], **XVIII** [14].

The mixture of isomeric aldehydes **XXIV** and **XXV** was separated by column chromatography on alumina, eluent hexane–diethyl ether with increasing fraction of the latter. *Exo* isomer **XXIV** was isolated 98% pure. The spectral properties of *endo* isomer **XXV** were studied using a fraction containing 43% of this isomer.

2-(3,3-Dimethylbicyclo[2.2.1]hept-2-*exo*-yl)pent-4-enal (XXIV). ^{1}H NMR spectrum, δ, ppm: 0.98 s and 1.02 s (6H, $2CH_3$), 1.56 d and 1.92 d (2H, isocamphane C^7H_2, J 9 Hz), 1.86 d (1H, isocamphane *endo*-HC^2, J 7.5 Hz), 2.05–2.45 m (5H, isocamphane bridging protons, aldehyde C^2H and C^3H_2), 5.02 d.d (1H, $=C^5H$, $J_{5,5'}$ 2, $J_{4,5}$ 10.5 Hz), 5.20 d.d (1H, $=C^5H$, $J_{5,5'}$ 2, $J_{4,5'}$ 16 Hz), 5.98 d.d (1H, CH=C, $J_{4,5}$ 10.5, $J_{4,5'}$ 16 Hz), 9.32 (1H, CHO).

2-(3,3-Dimethylbicyclo[2.2.1]hept-2-*endo*-yl)-pent-4-enal (XXV). ^{1}H NMR spectrum, δ, ppm: 0.97 s and 1.00 s (6H, $2CH_3$), 1.52 d and 1.73 d (2H, isocamphane C^7H_2, J 9.5 Hz), 2.19–2.24 m (1H, isocamphane *exo*-HC^2), 2.11–2.58 m (5H, isocamphane bridging fragments, aldehyde C^2H and C^3H_2), 5.06–5.18 m (2H, $=C^5H_2$), 5.92 d.d (1H, CH=C, $J_{4,5}$ 10, $J_{4,5'}$ 17 Hz), 9.28 (1H, CHO).

6-Methylene-*p*-menta-2,8-diene (XVI). By the procedure in [15] we obtained 6-(tosyloxymethyl)isolimonene and converted it to a tertiary amine by the procedure in [16]. The amine was oxidized by the procedure in [17], and the resulting *N*-oxide was decomposed by the procedure in [18]. Yield 52% per taken alcohol. The conditions of preparation of tosylate, amine, and *N*-oxide, as well as of decomposition of the latter excluded their isomerization. ^{1}H NMR spectrum, δ, ppm: 0.99 d (3H, CCH_3, J 7.5 Hz), 1.68 s (3H, $=CCH_3$), 2.02–2.12 m (2H, $>CH_2$), 2.49–2.60 (2H, methine protons on C^1 and C^4), 4.85 s and 4.96 s (2H, isopropenyl methylene protons), 4.80–5.03 m (2H, semicyclic methylene group), 5.46 d and 5.55 d (2H, vinyl protons, J 4 Hz).

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