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Functionalization of the Methyl Ketone Fragment in 1-[(1*S*,3*R*)-2,2-Dimethyl-3-(2-methoxymethyloxyethyl)cyclopropyl]-2-propanone

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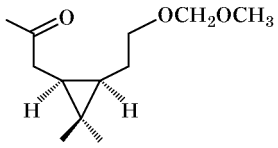
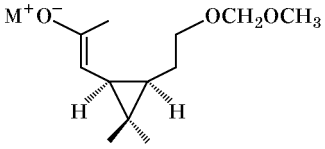
Abstract—Deprotonation of 1-[(1*S*,3*R*)-2,2-dimethyl-3-(2-methoxymethyloxyethyl)cyclopropyl]-2-propanone with lithium diisopropylamide in THF at –78°C and subsequent treatment of the resulting enolate with Me_3SiCl yielded mainly the corresponding terminal silyl enol ether. The condensation of intermediate enolate with benzaldehyde regioselectively afforded a mixture of the corresponding aldol and its dehydration product. The reactions of the title ketone with NBS, as well as of the silyl enol ethers derived therefrom with I_2, led to formation of mixtures of products via opening of the cyclopropane ring.

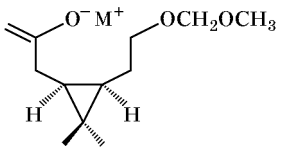
While studying the synthesis of geminal dimethyl-substituted carba analogs of epothilons from 3-carene [1, 2] we have encountered with some difficulties at the stage of selective functionalization of the methyl group of the carbonyl fragment in compound **I** [3]. These difficulties arise from an appreciable CH acidity of the methylene group located between the carbonyl and cyclopropyl fragment, which initiates side rearrangement processes accompanied by opening of the cyclopropane ring [4–6].



I



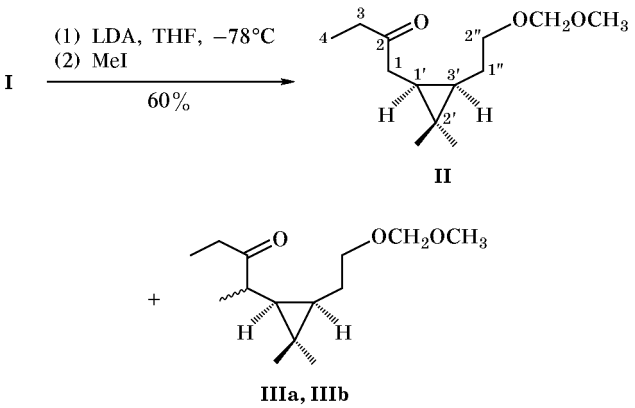
IA



IB

Although enolate **IA** should be sufficiently stable from the viewpoint of thermodynamics, *cis*-arrangement of the substituents in the cyclopropane ring and steric hindrances favor electrophilic attack on enolate **IB** under conditions of kinetic control [7]. Enolates generated from ketone **I** were brought into reactions with methyl iodide and chlorotrimethylsilane. Deprotonation of ketone **I** with lithium diisopropyl amide (LDA) in THF at –78°C, followed by addition of methyl iodide (1 h at –78°C and 1 h at 20°C) gave an almost equimolar mixture of compounds **II**, **IIIa**, and **IIIb** (according to the ^1H NMR data) which we failed to separate by chromatography on silica gel (Scheme 1).

Scheme 1.



These results indicate preferential formation of enolate **IB** and subsequent alkylation of the methyl

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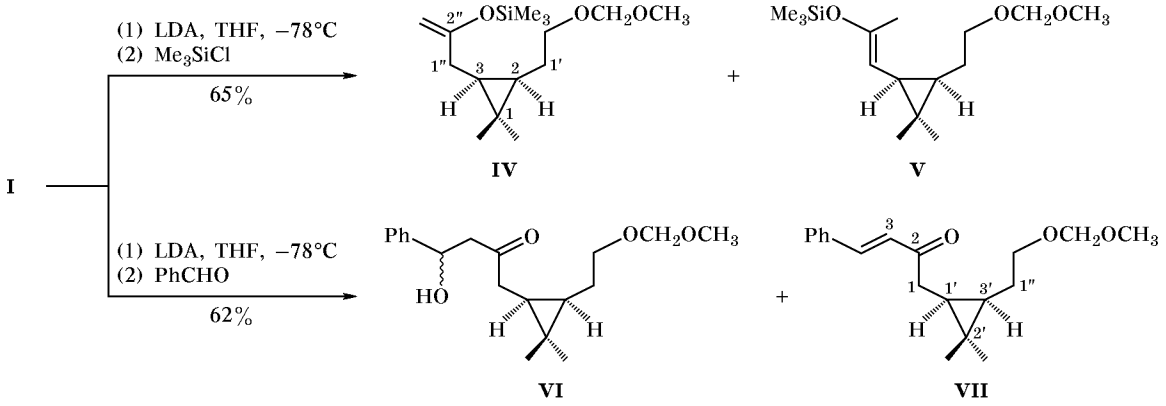
Scheme 2.

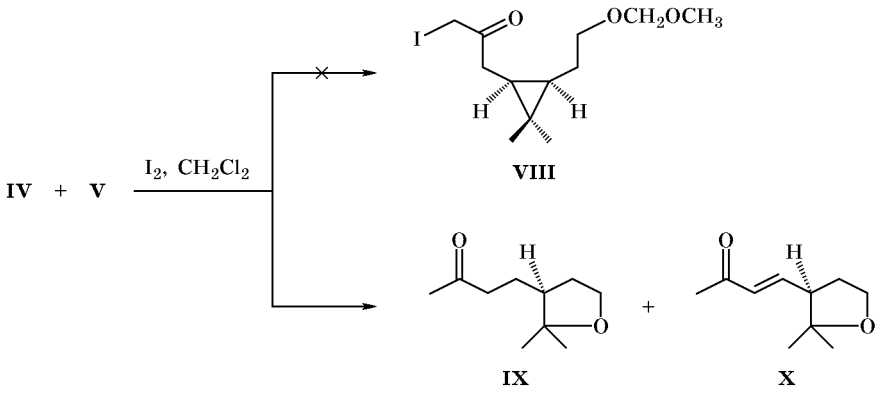


group. Epimeric compounds **IIIa** and **IIIb** are likely to be formed as a result of secondary metalation of ketone **II** with excess enolate **IB**; in this case, the internal methylene group (C^1H_2) undergoes alkylation. No O-alkylation products were detected in the reaction mixture; such compounds did not appear even on addition of HMPA which is known to favor formation of enol ethers.

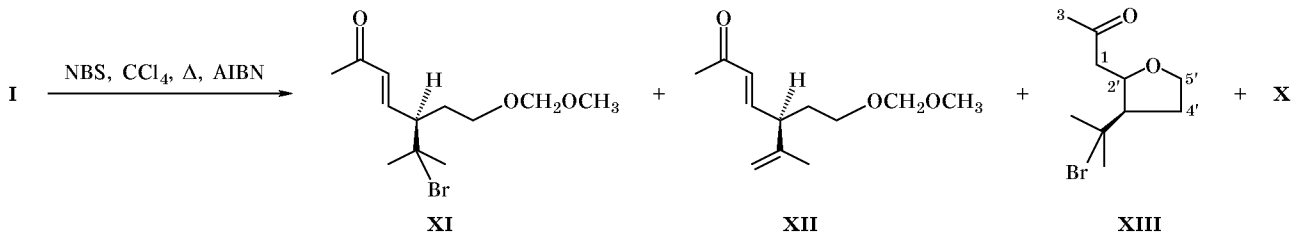
We were able to estimate the ratio of intermediate enolates more reliably by reacting them with a highly active hard electrophile, chlorotrimethylsilane, under conditions of kinetic control. The resulting mixture of trimethylsilyl enol ethers **IV** and **V** was purifed by chromatography on silica gel; their overall yield was 65%, and the ratio **IV**:**V** was equal to 6:1 (^{1}H NMR data). Better results were obtained while studying the condensation of the enolates derived from **I** with benzaldehyde. The reaction was highly regioselective, and we isolated a mixture of aldol **VI** and its dehydration product **VI** at a ratio of about 1:1 (^{1}H NMR) (Scheme 2).

Thus we have demonstrated the possibility for generation of terminal enolates from ketone **I**. The isolation of silyl enol ether **IV** opens the way to further more profound oxidative functionalization of the methyl group in **I**. In particular, we examined the

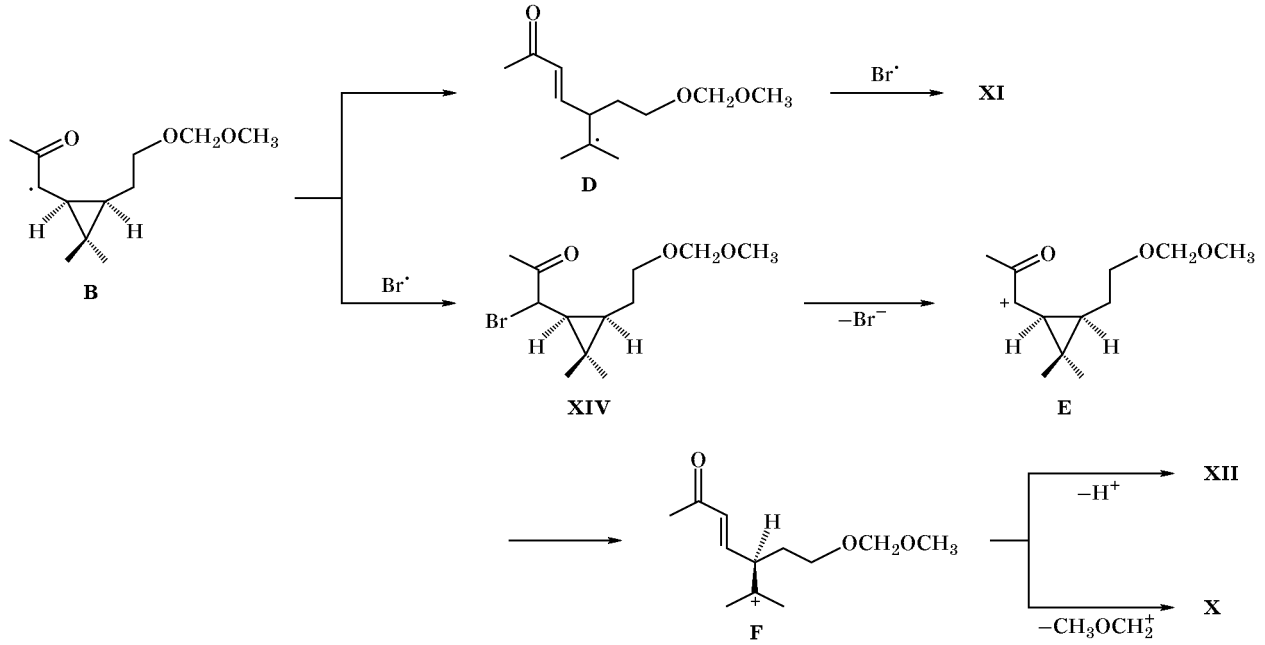
Scheme 3.



Scheme 4.



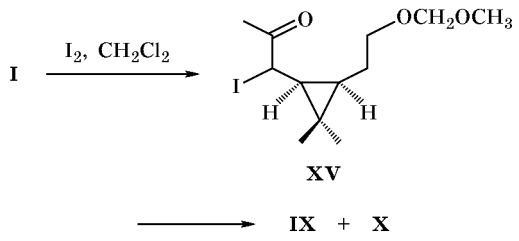
Scheme 5.



reaction of mixture **IV**/**V** with molecular iodine with a view to obtain α-iodo ketone **VIII**. The reaction was smooth, and it resulted in formation of a chromatographically (TLC) homogeneous substance which however appeared to be (according to spectral data) a mixture of tetrahydrofuran derivatives **IX** and **X** at a ratio of 4:1 (^{1}H NMR) (Scheme 3). In order to interpret the observed pattern we examined radical bromination of ketone **I** with *N*-bromosuccinimide, which should follow an analogous mechanism. The bromination afforded a mixture of products which were separated by column chromatography on silica gel. We isolated two fractions, each containing two structurally related products, **XI**/**XII** and **XIII**/**X** (Scheme 4). A probable mechanism of the bromination process is shown in Scheme 5. Radical initiation with NBS + AIBN gives rise to radicals **B** which are capable of both taking up bromine atom to give α-bromo ketone **XIV** and undergoing rearrangement to new radical **D** via homolytic cleavage of the C^1-C^2 bond. Radical **D** takes up bromine atom to afford tertiary bromo derivative **XI**. α-Bromo ketone **XIV** (on heating in CCl_4) loses bromide ion, yielding cation **E**. Heterolytic opening of the cyclopropane ring in **E** gives carbocation **F** which can be stabilized along two concurrent pathways: elimination of proton leads to dienone **XII**, and intramolecular cyclization with loss of the methoxymethyl cation yields tetrahydrofuran derivative **X** (for intramolecular cyclizations of allyl ketones derived from cyclopropanes, see [8]). The formation of saturated tetrahydrofuran derivative **XIII** may be explained by partial removal of the methoxymethyl protecting group from ether **XI** (or **I**) and subsequent cyclization of the intermediate alcohol according to Michael.

The results of studying the reaction of ketone **I** with NBS allowed us to elucidate to some extent the situation observed in the iodination of silyl enol ethers **IV**/**V**. The presence of enone **X** among the products of both reactions suggests similar mechanisms of these processes. Therefore, we may presume intermediate formation of α-iodo ketone **XV** in the reaction of **IV**/**V** with I_2. Heterolytic dissociation of the C–I bond in **XV** (like in α-bromo ketone **XIV**) should afford compound **X**. The possibility for formation of **XV** also follows from the results of direct iodination of cyclopropylmethyl ketone **I**. The reaction readily occurred in methylene chloride and led to a mixture of tetrahydrofurans **IX** and **X** whose ratio (4:1) was the same as in the iodination of silyl enol

Scheme 6.



ether mixture **IV**/**V** (Scheme 6). However, particular steps of formation of both α-iodo ketone **XV** and tetrahydrofuran derivatives **IX** and **X** from enol ethers **IV** and **V** are not understood completely.

EXPERIMENTAL

The IR spectra were recorded on UR-20 and Specord-80 spectrometers from samples prepared as thin films or mulls in mineral oil. The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AM-300 spectrometer at 300.13 and 75.47 MHz, respectively, using tetramethylsilane as internal reference. The optical rotations were measured on a Perkin–Elmer 141 polarimeter. The mass spectrum (electron impact, 70 eV) was obtained on a Varian MAT CH-5 mass spectrometer.

1-[(1*S*,3*R*)-2,2-Dimethyl-3-(2-methoxymethyloxyethyl)cyclopropyl]-2-butanone (II) and (2*RS*)-2-[(1*S*,3*R*)-2,2-dimethyl-3-(2-methoxymethyloxyethyl)cyclopropyl]-3-pentanone (IIIa/IIIb). A solution of butyllithium in hexane, 0.42 ml (1.68 mmol, 4 M), was added dropwise to a solution of 0.19 g (1.68 mmol) of diisopropylamine in 5 ml of anhydrous THF while stirring under argon at –78°C. The mixture was stirred for 10 min at –78°C, allowed to warm up to 0°C, and stirred for 30 min at that temperature. The mixture was cooled again to –78°C, and a solution of 0.3 g (1.40 mmol) of compound **I** in 5 ml of anhydrous THF was added dropwise over a period of 5 min. The mixture was stirred for 1 h at –78°C, 0.48 g (3.36 mmol) of methyl iodide was added (at –78°C), and the mixture was stirred for 30 min. The cooling bath was removed, and the mixture was stirred for 1 h at room temperature. When the reaction was complete (TLC), the mixture was cooled to 0°C, and 10 ml of a saturated solution of NH_4Cl was added dropwise. Tetrahydrofuran was evaporated, the residue was treated with chloroform (3 × 10 ml), and the extracts were combined, dried over $MgSO_4$, and evaporated. The residue was purified by column chromatography on silica gel using ethyl acetate–petroleum ether (1 : 6) as eluent. We isolated 0.19 g (60%) of a mixture of compounds **II**, **IIIa**, and **IIIb** which could not be separated by chromatography on silica gel; the ratio of epimers **IIIa** and **IIIb** was about 1 : 1 (according to the ^{1}H NMR data). IR spectrum, ν, cm^{-1}: 922, 1036, 1108, 1150, 1378, 1714.

Compound **II**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.86 s and 1.00 s (6H, CH_3), 1.02 t (3H, CH_3, J = 7.0 Hz), 3.31 s (3H, OCH_3), 4.58 s (2H, OCH_2O). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 7.74 (C^4H_3), 15.24 (*trans*-CH_3), 16.81 ($C^{2'}$), 22.76 ($C^{1'}$), 22.30 ($C^{3'}$), 25.36 ($C^{1''}$), 28.78 (*cis*-CH_3), 35.33 (C^3), 37.98 (C^1), 54.92 (OCH_3), 67.68 ($C^{2''}$), 96.22 (OCH_2O), 211.38 (C=O).

Epimers **IIIa**/**IIIb**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.87 s (0.94) (3H, CH_3), 1.00 s (1.02) (3H, CH_3), 1.08 d (1.09) (3H, CH_3, J = 6.0 Hz), 1.02 t (3H, CH_3, J = 7.0 Hz), 3.28 s (3.29) (3H, OCH_3), 4.54 s (4.56) (2H, OCH_2O). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 7.60 (C^4H_3), 14.68 (14.82) (*trans*-CH_3), 16.64 (16.81) ($C^{2'}$), 17.42 (17.62) (C^1**C**H_3), 21.09 ($C^{3'}$), 23.48 ($C^{1'}$), 24.82 (24.99) ($C^{1''}$), 29.30 (29.69) (*cis*-CH_3), 32.33 (32.84) (C^3), 42.96 (43.79) (C^1), 54.92 (OCH_3), 67.79 ($C^{2''}$), 96.22 (OCH_2O), 214.84 (215.04) (C=O).

(1*R*,3*S*)-1-(2-Methoxymethyloxyethyl)-2,2-dimethyl-3-(2-trimethylsiloxy-2-propenyl)cyclopropane (IV) and (1*R*,3*S*)-1-(2-methoxymethyloxyethyl)-2,2-dimethyl-3-(2-trimethylsiloxy-1-propenyl)cyclopropane (V). A solution of 0.3 g (1.40 mmol) of compound **I** in 5 ml of anhydrous tetrahydrofuran was added dropwise over a period of 5 min to a solution of lithium diisopropylamide (prepared as described above) while stirring at –78°C. The mixture was stirred for 1 h at –78°C, a solution of 0.37 g (3.36 mmol) of Me_3SiCl in 3 ml of THF was added at that temperature, and the mixture was stirred for 30 min. The cooling bath was removed, and the mixture was stirred for 1 h at room temperature. When the reaction was complete (TLC), 10 ml of water was added at 0°C, tetrahydrofuran was evaporated, the inorganic precipitate was filtered off, and the aqueous phase was extracted with chloroform (3 × 10 ml). The extracts were combined, dried over $MgSO_4$, and evaporated. The residue was purified by column chromatography on silica gel using ethyl acetate–petroleum ether (1 : 9) as eluent. We isolated 0.26 g (65%) of a mixture of compounds **IV** and **V** at a ratio of 6 : 1 (according to the ^{1}H NMR data) as an oily substance.

Compound **IV**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.16 s (3H, $OSiMe_3$), 0.51 m and 0.62 m (1H each, 2-H, 3-H), 0.89 s and 1.02 s (6H, CH_3), 1.51 m (2H, 1′-H_2), 1.88 d.d (1H, J = 8.0, 16.0 Hz) and 1.94 d.d (1H, 1″-H_2, J = 8.0, 16.0 Hz), 3.30 s (3H, OCH_3), 3.49 d.t (2H, OCH_2, J = 1.54, 6.0 Hz), 4.04 s and 4.11 s (1H each, =CH_2), 4.57 s (2H, OCH_2O). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 0.02 ($SiMe_3$), 14.57 and 29.05 (CH_3), 16.66 (C^1), 22.82 and 23.71 (C^2, C^3), 24.90 ($C^{1'}$), 31.42 ($C^{1''}$), 54.83 (OCH_3), 67.99 (OCH_2), 89.68 (=CH_2), 96.22 (OCH_2O), 159.7 ($C^{2''}$).

Compound **V**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.13 s (3H, $OSiMe_3$), 0.62 m and 0.83 m (1H each, 2-H, 3-H), 0.87 s and 1.04 s (3H each, CH_3), 1.21 m (2H, 1′-H_2), 1.73 s (3H, $C^{3'}H_3$), 3.30 s (3H, OCH_3), 3.49 t (2H, OCH_2, J = 6.0 Hz), 4.06 d (2H, =CH, J = 7.2 Hz), 4.57 s (2H, OCH_2O). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 0.13 ($SiMe_3$), 14.06 and 28.71 (CH_3), 18.37 (CH_3), 18.97 (C^1), 24.28 and 24.90 (C^2, C^3), 25.5 ($C^{1'}$), 54.83 (OCH_3), 67.71 ($C^{2'}$), 96.22 (OCH_2O), 103.21 ($C^{1''}$), 150.48 ($C^{2''}$).

(4*RS*)-4-Hydroxy-1-[(1*S*,3*R*)-2,2-dimethyl-3-(2-methoxymethyloxyethyl)cyclopropyl]-4-phenyl-2-butanone (VI) and 1-[(1*S*,3*R*)-2,2-dimethyl-3-(2-methoxymethyloxyethyl)cyclopropyl]-4-phenyl-3-buten-2-one (VII). A solution of 0.5 g (2.33 mmol) of compound **I** in 8 ml of anhydrous THF was added dropwise over a period of 5 min to a solution of lithium diisopropylamide (prepared as described above) while stirring at –78°C. The mixture was stirred for 1 h at –78°C, a solution of 0.37 g (3.50 mmol) of benzaldehyde in 3 ml of THF was added, and the mixture was stirred for 30 min at that temperature. The cooling bath was removed, and the mixture was stirred for 3 h at room temperature, the progress of the reaction being monitored by TLC. When the reaction was complete, 10 ml of water was added at 0°C, tetrahydrofuran was evaporated, and the precipitate was filtered off. The aqueous layer was treated with chloroform (3 × 15 ml), the extracts were combined, dried over $MgSO_4$, and evaporated, and the residue was purified by column chromatography on silica gel using ethyl acetate–petroleum ether (1:7) as eluent. We isolated 0.23 g (32%) of compound **VI** and 0.2 g (30%) of **VII**.

Compound **VI**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.6 q (1H, J = 16.0 Hz) and 0.83 q (1H, 1′-H, 3′-H, J = 16.4 Hz), 0.88 s and 1.08 s (6H, CH_3), 1.46 m (2H, 1″-H_2), 2.36 m (2H, 1-H_2), 2.74 d (1H, J = 16.7 Hz) and 2.88 d.d (1H, 3-H_2, J = 9.0, 16.9 Hz), 3.48 t (2H, OCH_2, J = 7.0 Hz), 3.88 br.s (1H, OH), 4.23 s (2H, OCH_2O), 5.14 m (1H, 4-OH), 7.33 m (5H, C_6H_5). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.76 and 28.57 (CH_3), 16.67 ($C^{2'}$), 20.56 and 22.74 ($C^{1'}$, $C^{3'}$), 24.76 ($C^{1''}$), 39.29 (C^1), 50.67 ($C^{3'}$), 54.80 (OCH_3), 67.58 ($C^{2''}$), 69.82 (C^4), 95.99 (OCH_2O), 125.41, 127.35, 128.25 (C^o, C^p, C^m), 143.01 (C^i), 210.95 (C=O).

Compound **VII**. $[\alpha]_D^{20}$ = –4.45° (c = 3.30, MeOH). IR spectrum, ν, cm^{-1}: 700, 754, 922, 988, 1036, 1108, 1150, 1336, 1378, 1450, 1576, 1612, 1654, 1714. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.64 q (1H, J = 16.1 Hz) and 0.99 m (1H, 1′-H, 3′-H), 0.94 s and 1.08 s (6H, CH_3), 1.54 d.d (2H, 1″-H_2, J = 7.03, 14.1 Hz), 3.32 s (3H, OCH_3), 3.52 t (2H, OCH_2, J = 7.0 Hz), 4.59 s (2H, OCH_2O), 6.72 d.d (1H, J = 11.10, 16.3 Hz) and 7.55 d (1H, CH=CH, J = 10.9 Hz), 7.35 m and 7.51 m (5H, C_6H_5). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 15.02 and 29.66 (CH_3), 16.93 ($C^{2'}$), 21.31 and 22.97 ($C^{1'}$, $C^{3'}$), 25.12 ($C^{1''}$), 36.85 (C^1), 54.94 (OCH_3), 67.75 ($C^{2''}$), 96.24 (OCH_2O), 125.59, 127.03, 128.15, 128.84, 129.59, 134.68 (C_{arom}), 130.29 (C^3), 142.05 (C^4), 198.89 (C=O). Found, %: C 75.90; H 8.64. $C_{19}H_{26}O_3$. Calculated, %: C 75.46; H 8.67.

4-[(3*S*)-2,2-Dimethyltetrahydrofuran-3-yl]-2-butanone (IX) and (*E*)-4-[(3*R*)-2,2-dimethyltetrahydrofuran-3-yl]-3-buten-2-one (X). A solution of 0.1 g of a mixture of compounds **IV** and **V** in 2 ml of methylene chloride was added dropwise with stirring to a solution of 0.05 g (0.192 mmol) of molecular iodine in 3 ml of methylene chloride. The mixture was stirred for 3 h (the progress of the reaction was monitored by TLC), diluted with 10 ml of methylene chloride, and washed in succession with saturated solutions of $Na_2S_2O_3$ and NaCl. The organic layer was separated, dried over $MgSO_4$, and evaporated. We thus isolated 0.04 g of a mixture of compounds **IX** and **X** at a ratio of ~4:1 (according to the ^{1}H NMR data). IR spectrum, ν, cm^{-1}: 1036, 1156, 1360, 1618, 1666, 1708. Mass spectrum, *m*/*z*: 170 $[M_1]^+$, 168 $[M_2]^+$, 155 $[M_1 - CH_3]^+$, 153 $[M_2 - CH_3]^+$, 112 $[M_1 - CH_3C(OH)=CH_2]^+$, 110 $[M_2 - CH_3C(OH)=CH_2]^+$, 97 $[M_1 - CH_3 - CH_3C(OH)=CH_2]^+$, 95 $[M_2 - CH_3 - CH_3C(OH)=CH_2]^+$, 83, 82, 71, 69, 59, 58 $[CH_3C(OH)=CH_2]^+$, 55, 43 $[CH_3C\equiv O]^+$ (100%).

Compound **IX**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.01 s and 1.24 s (6H, CH_3), 1.40–1.75 m (4H, 1-H_2, 4′-H_2), 2.00–2.10 m (1H, 3′-H), 2.15 s (3H, CH_3), 2.45 m (2H, 2-H_2), 3.70–3.90 m (2H, 5′-H_2). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 22.00 and 27.61 (CH_3), 24.34 (C^1), 30.01 (C^4), 31.90 ($C^{4'}$), 43.07 (C^2), 48.01 ($C^{3'}$), 64.82 ($C^{5'}$), 81.70 ($C^{2'}$), 206.53 (C^3).

Compound **X**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.05 s and 1.23 s (6H, CH_3), 2.22 s (3H, C^4H_3), 6.09 d (1H, 2-H, J = 16.0 Hz), 6.63 d.d (1H, 1-H, J = 7.0, 16.0 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 22.79 and 26.96 (CH_3), 31.60 ($C^{4'}$), 33.02 (C^4), 51.82 ($C^{3'}$), 65.30 ($C^{5'}$), 82.55 ($C^{2'}$), 131.77 (C^2), 146.30 (C^1), 197.88 (C^3).

(3*E*,5*R*)-6-Bromo-6-methyl-5-(2-methoxymethyloxyethyl)-3-hepten-2-one (XI), (3*E*)-6-methyl-5-(2-methoxymethyloxyethyl)-3,6-heptadien-2-one (XII),

and 1-[(3*R*)-[3-(1-bromo-1-methylethyl)tetrahydrofuran-2-yl]-2-propanone (XIII). A solution of 0.2 g (1.06 mmol) of compound **I**, 0.26 g (1.16 mmol) of *N*-bromosuccinimide, 0.002 g of azobis(isobutyronitrile) (AIBN), and 5 ml of CCl_4 was heated for 3 h under reflux (the progress of the reaction was monitored by TLC). The mixture was cooled, diluted with 10 ml of $CHCl_3$, and washed with an aqueous solution of NaCl. The organic phase was dried over $MgSO_4$ and evaporated, and the residue was subjected to column chromatography on silica gel using ethyl acetate–petroleum ether (1:6) as eluent. We isolated 0.11 g of a mixture of compounds **XI** and **XII** at a ratio of 3:2 (^{1}H NMR) and 0.035 g of a mixture of compounds **XIII** and **X** at a ratio of 3:1 (^{1}H NMR). IR spectrum, ν, cm^{-1}: mixture **XI**/**XII**: 520, 832, 1036, 1084, 1150, 1366, 1654, 1714; **XIII**/**X**: 1036, 1150, 1366, 1654, 1702.

Compound **XI**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.63 s and 1.78 s (6H, CH_3), 2.10–2.40 m (3H, CH, CH_2), 2.22 s (3H, C^1H_3), 3.30 s (3H, OCH_3), 3.35 m and 3.50 m (1H each, OCH_2), 4.54 d (1H, J = 6.5 Hz) and 4.57 d (1H, OCH_2O, J = 6.5 Hz), 6.06 d (1H, 3-H, J = 16.0 Hz), 6.62 d.d (1H, 4-H, J = 9.7, 16.0 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 26.89 (CH_3), 30.76 ($C^{1'}$), 32.82 (C^1), 52.26 (C^5), 55.11 (OCH_3), 64.82 ($C^{2'}$), 67.19 (CBr), 96.30 (OCH_2O), 130.79 (C^3), 146.67 (C^4), 197.80 (C^2).

Compound **XII**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.68 s (3H, CH_3), 2.19 s (3H, C^1H_3), 3.43 t (2H, OCH_2, J = 6.5 Hz), 4.50 s (2H, OCH_2O), 4.75 s and 4.83 s (2H, $=CH_2$), 6.03 d (1H, 3-H, J = 16.0 Hz), 6.60 d.d (1H, 4-H, J = 8.0, 16.0 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 19.90 (CH_3), 31.71 ($C^{1'}$), 32.96 (C^1), 46.08 (C^5), 55.11 (OCH_3), 64.82 ($C^{2'}$), 96.30 (OCH_2O), 112.62 ($CH_2=$), 144.42 (=**C**Me), 133.92 (C^3), 149.08 (C^4), 198.28 (C^2).

Compound **XIII**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.76 s (6H, CH_3); 1.89 m (1H), 2.06 m (1H), and 2.25 m (1H, 3′-H, 4′-H_2); 2.20 s (3H, C^3H_3); 2.70 d.d (2H, C^1H_2, J = 1.5, 7.0 Hz); 3.83 m (2H, OCH_2); 4.40 q (1H, 2′-H, J = 7.0 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 30.47 ($C^{4'}$), 30.64 (C^3), 31.99 and 33.18 (CH_3), 49.73 (C^1), 57.48 ($C^{3'}$), 65.36 (CBr), 67.24 ($C^{5'}$), 77.64 ($C^{2'}$), 206.92 (C=O).

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