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Transformation of Carboxylic Acid Esters into 2-Substituted Allyl Halides through Tertiary Cyclopropyl Sulfonates. Application in the Synthesis of (±)-Ipsenol and (±)-Ipsdienol, Components of *Ips typographus* Spark Beetle Pheromone

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Abstract—Cyclopropanation of the ester group in ethyl 3-chloropropanoate and subsequent cleavage of the three-membered carbocycle in intermediate 1-(2-chloroethyl)cyclopropyl methanesulfonate gave 2-bromomethyl-4-chlorobut-1-ene, and the latter was used as key intermediate in the synthesis of racemic ipsenol and ipsdienol which are components of *Ips typographus L*. European spruce spark beetle pheromone.

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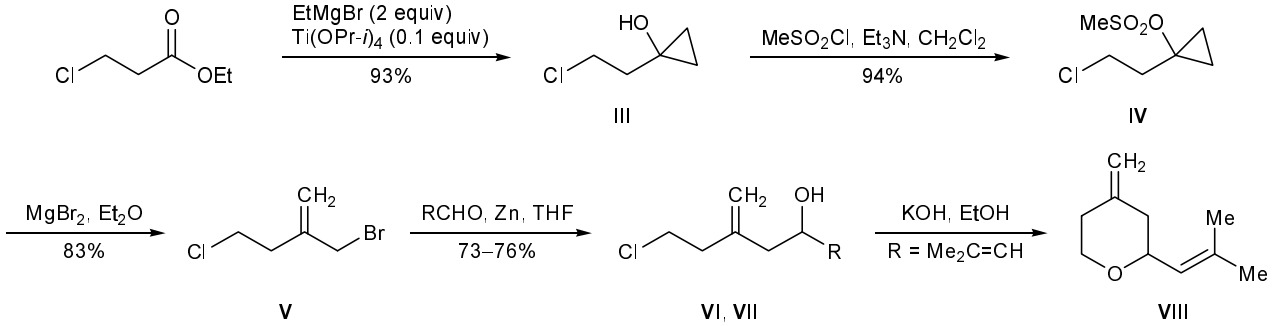
Cyclopropanol derivatives are widely used as intermediate products in organic synthesis due to their accessibility and ability to undergo transformations with opening of the three-membered ring under mild conditions [1, 2]. The oxygen atom in these compounds activates heterolytic or homolytic cleavage of the adjacent carbon–carbon bond (C^1–C^2 or C^1–C^3) in the cyclopropane ring to give the corresponding carbonyl compounds or their synthetic equivalents, whereas dissociation of the C^2–C^3 bond is promoted by heterolytic cleavage of the carbon–oxygen bond, and it follows the cationic cyclopropyl–allyl isomerization pattern. On the basis of the latter process we have recently developed a convenient procedure for the preparation of 2-substituted allyl halides from tertiary cyclopropyl sulfonates by the action of magnesium, aluminum, or titanium halides [3, 4]. The developed procedure was applied to the synthesis of some natural compounds [5–7]. The present communication reports on the successful application of this approach to the synthesis of racemic ipsenol (**I**) and ipsdienol (**II**) which are components of the European spruce spark beetle (*Ips typographus L.*) pheromone [8–10].

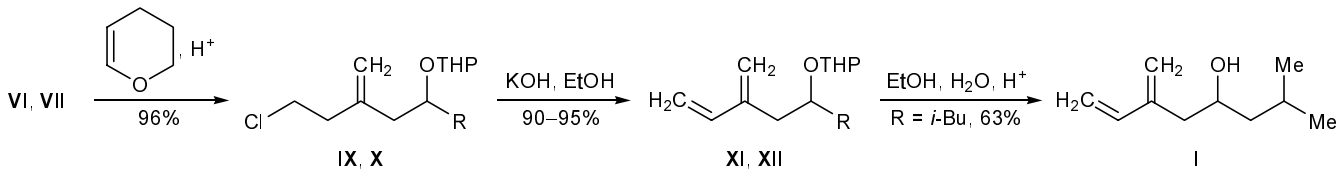
1-(2-Chloroethyl)cyclopropanol (**III**) was synthesized by cyclopropanation of ethyl 3-chloropropionate with ethylmagnesium bromide in the presence of titanium(IV) isopropoxide [11] and was converted into methanesulfonate **IV** according to standard procedure. Replacement of the sulfonate group in **IV** by the action of magnesium bromide gave substituted allyl bromide **V** in a good yield (Scheme 1). The latter was used to build up the ipsenol and ipsdienol carbon skeletons via reactions with 3-methylbutanal and 3-methylbut-2-enal, respectively, in the presence of metallic zinc in

Scheme 1.



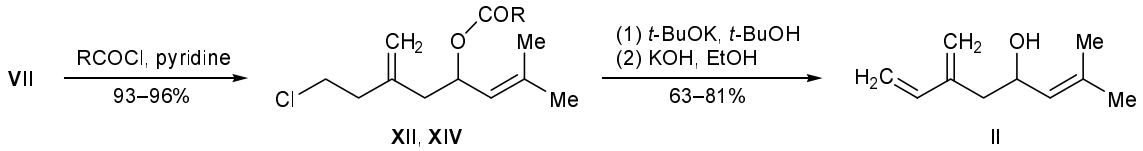
VI, R = *i*-Bu; **VII**, R = Me_2C=CH.

Scheme 2.



IX, **XI**, R = *i*-Bu; **X**, **XII**, R = Me_2C=CH.

Scheme 3.



XII, R = Ph; **XIII**, R = *i*-Bu; **XIV**, R = *t*-Bu.

boiling tetrahydrofuran. Chlorine-containing homoallyl alcohols **VI** and **VII** thus formed were isolated in good yields by vacuum distillation. Dehydrochlorination of compound **VII** by treatment with potassium hydroxide in boiling ethanol afforded 2-(2-methylprop-1-enyl)-4-methylidenetetrahydropyran (**VIII**) [12].

In order to force the dehydrochlorination process to produce conjugated diene systems, the hydroxy group in alcohols **VI** and **VII** was protected by tetrahydropyran-2-yl group according to standard procedure [13]. Treatment of cyclic acetals **IX** and **X** with potassium hydroxide in boiling ethanol gave 1,3-dienes **XI** and **XII** in high yields. By hydrolysis of acetal **XI** in boiling ethanol in the presence of 0.1 equiv of pyridinium *p*-toluenesulfonate we obtained ipsenol (**I**) (Scheme 2); its overall yield (calculated on the initial ethyl 3-chloropropanoate) was 30%.

However, we failed to effect analogous smooth deprotection of compound **XII**, and the desired ipsdienol (**II**) was not isolated. The use of different acid reagents, as well as of lithium chloride in aqueous dimethyl sulfoxide [14], led to formation of mixtures of solvolysis products or the reaction rate was too low. These obstacles were circumvented by protecting the hydroxy group in **VII** with an ester moiety and using a bulky base, potassium *tert*-butoxide, in the dehydrochlorination stage to avoid undesirable transesterification (Scheme 3). Under these conditions, compound **VIII** was formed in small amounts; in the series of benzoyloxy, isobutyryloxy, and pivaloyloxy derivatives **XII**–**XIV**, the fraction of tetrahydropyran **VIII** in the reaction products was 25, 10, and 3%, respectively, and compound **VIII** was readily separated from the target product (**II**) by distillation or column chromatography. The reaction of ester **XIV** with potassium hydroxide in ethanol resulted in formation of approximately equimolar amounts of ipsdienol (**II**) and compound **VIII**. The overall yield of ipsdienol (**II**) through esters **XII**–**XIV** was 34–42%.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were obtained from solutions in chloroform-*d* on a Bruker AC-400 spectrometer at 400 and 100 MHz, respectively. The IR spectra were measured from solutions in carbon tetrachloride on a Specord 75 IR spectrophotometer. The mass spectra (electron impact, 70 eV) were recorded on a Hewlett–Packard 5890/5972 GC–MS system. Diethyl ether and tetrahydrofuran were dried and distilled over metallic sodium.

2-Bromomethyl-4-chlorobut-1-ene (V). A solution of 25.7 g (130 mmol) of 1-(2-chloroethyl)cyclopropyl methanesulfonate (**IV**) [3] in 40 ml of anhydrous diethyl ether was added dropwise under stirring to a solution of $MgBr_2$ prepared from 6.24 g (260 mmol) of magnesium turnings and 48.90 g (260 mmol) of 1,2-dibromoethane in 225 ml of anhydrous diethyl ether. The mixture was heated at the boiling point for 5 h under stirring, cooled, and treated with 250 ml of 10% aqueous ammonium chloride. The organic layer was separated, washed with water (2 × 50 ml) and a saturated solution of sodium chloride (100 ml), and dried over $MgSO_4$. The solvent was distilled off under atmospheric pressure, and the residue was distilled under reduced pressure (water-jet pump). Yield 19.71 g (83%), bp 75–80°C (15 mm). IR spectrum, ν, cm^{-1}: 1650, 665. ^{1}H NMR spectrum, δ, ppm: 2.69 t (2H, *J* =

7 Hz), 3.67 t (2H, J = 7 Hz), 3.99 s (2H), 5.07 s (1H), 5.31 s (1H). ^{13}C NMR spectrum, δ_C, ppm: 35.85, 36.27, 42.07, 117.61, 141.55.

Homoallyl alcohols VI and VII (*general procedure*). Zinc dust, 6.95 g (107 mmol), was added to a solution of 13.03 g (71 mmol) of allyl bromide **V** and 75 mmol of 3-methylbutanal or 3-methylbut-2-enal in 65 ml of anhydrous tetrahydrofuran. The mixture was stirred for 20 min on heating under reflux, the solvent was distilled off under reduced pressure, and 65 ml of diethyl ether and 30 ml of a saturated aqueous solution of ammonium chloride were added to the residue. The mixture was filtered, and the organic phase was separated, washed with a saturated solution of NH_4Cl (3×25 ml), and dried over $MgSO_4$. The solvent was distilled off, and the residue was distilled under reduced pressure to isolate compound **VI** or **VII**.

2-(2-Chloroethyl)-6-methylhept-1-en-4-ol (VI). Yield 9.87 g (73%), bp 98–104°C (4 mm). IR spectrum, ν, cm^{-1}: 3555, 1645. ^{1}H NMR spectrum, δ, ppm: 0.91 d (3H, J = 7 Hz), 0.93 d (3H, J = 7 Hz), 1.23 d.d.d (1H, J_1 = 14, J_2 = 9, J_3 = 4 Hz), 1.42 d.d.d (1H, J_1 = 14, J_2 = 9, J_3 = 6 Hz), 1.70 s (1H), 1.74–1.85 m (1H), 2.08 d.d (1H, J_1 = 14, J_2 = 9 Hz), 2.22 d.d (1H, J_1 = 14, J_2 = 4 Hz), 2.52 t (2H, J = 7 Hz), 3.60–3.66 m (2H), 3.74–3.83 m (1H), 4.96–4.99 m (2H). ^{13}C NMR spectrum, δ_C, ppm: 22.04, 23.36, 24.62, 38.83, 42.51, 44.72, 46.34, 67.13, 114.78, 142.71. Found, %: C 63.15; H 9.95. $C_{10}H_{19}ClO$. Calculated, %: C 62.98; H 10.04.

2-(2-Chloroethyl)-6-methylhepta-1,5-dien-4-ol (VII). Yield 10.18 g (76%), bp 91–97°C (2–3 mm). IR spectrum, ν, cm^{-1}: 3615, 1655. ^{1}H NMR spectrum, δ, ppm: 1.63 s (1H), 1.69 d (3H, J = 1 Hz), 1.72 d (3H, J = 1 Hz), 2.16–2.30 m (2H), 2.53 t (2H, J = 7 Hz), 3.63 t (2H, J = 7 Hz), 4.48 t.d (1H, J_1 = 8, J_2 = 5 Hz), 4.95–4.97 m (1H), 4.98–5.00 m (1H), 5.15–5.20 m (1H). ^{13}C NMR spectrum, δ_C, ppm: 18.12, 25.58, 38.97, 42.46, 44.02, 66.49, 114.65, 127.25, 135.23, 142.30. Found, %: C 63.85; H 8.96. $C_{10}H_{17}ClO$. Calculated, %: C 63.65; H 9.08.

4-Methylidene-2-(2-methylprop-1-enyl)tetrahydro-2*H*-pyran (VIII). A solution of 3.01 g (16 mmol) of compound **VII** and 2.25 g (40 mmol) of potassium hydroxide in 30 ml of 96% ethanol was heated for 2 h under reflux. The mixture was cooled, diluted with 100 ml of water, and extracted with petroleum ether (3×15 ml). The extracts were combined, washed with water (3×15 ml) and a saturated solution of sodium chloride (15 ml), and dried over $MgSO_4$. The solvent was distilled off, and the residue was purified by column chromatography on silica gel (15 g) using first petroleum ether and then petroleum ether–diethyl ether (20:1) as eluent. We isolated 1.18 g (48%) of compound **VIII** as a yellowish oily liquid. IR spectrum: ν 1650 cm^{-1}. ^{1}H NMR spectrum, δ, ppm: 1.67–1.69 m (3H), 1.72–1.74 m (3H), 2.04–2.21 m (3H), 2.25–2.35 m (1H), 3.42 d.d.d (1H, J_1 = 12, J_2 = 11, J_3 = 3 Hz), 3.96 d.d.d (1H, J_1 = 11, J_2 = 8, J_3 = 3 Hz), 4.06 d.d.d (1H, J_1 = 12, J_2 = 6, J_3 = 2 Hz), 4.71–4.75 m (2H), 5.18–5.22 m (1H). ^{13}C NMR spectrum, δ_C, ppm: 18.38, 25.65, 34.99, 41.29, 68.39, 75.78, 108.36, 125.63, 136.05, 144.57.

Tetrahydropyranyl derivatives IX and X (*general procedure*). Homoallyl alcohol **VI** or **VII**, 13 mmol, was dissolved in 25 ml of anhydrous methylene chloride, and 1.79 ml (20 mmol) of 3,4-dihydro-2*H*-pyran and 320 mg (1.3 mmol) of pyridinium *p*-toluenesulfonate were added to the solution. The mixture was stirred for 3 h at room temperature and treated with 10 ml of a saturated solution of $NaHCO_3$. The organic layer was separated, washed with water (30 ml) and an aqueous solution of NaCl (30 ml), and dried over $MgSO_4$. Removal of the solvent under reduced pressure gave compound **IX** or **X** as an equimolar mixture of diastereoisomers.

2-[1-Isobutyl-3-(2-chloroethyl)but-3-enyloxy]-tetrahydro-2*H*-pyran (IX). Yield 3.40 g (96%). IR spectrum, ν, cm^{-1}: 1645. ^{1}H NMR spectrum, δ, ppm: 0.88 t (3H, J = 6 Hz), 0.89 t (3H, J = 6 Hz), 1.21–1.29 m (1H), 1.32–1.41 m (0.5H), 1.43–1.57 m (4.5H), 1.60–1.87 m (3H), 2.13 d.d (0.5H, J_1 = 14, J_2 = 6 Hz), 2.21–2.29 m (1H), 2.41 d.d (0.5H, J_1 = 14, J_2 = 6 Hz), 2.50 t (1H, J = 7 Hz), 2.54 t (1H, J = 7 Hz), 3.42–3.52 m (1H), 3.61 t (1H, J = 7 Hz), 3.64 t (1H, J = 7 Hz), 3.73–3.94 m (2H), 4.60–4.67 m (1H), 4.86–4.89 m (1H), 4.90 s (1H).

2-{1-[2-(2-Chloroethyl)prop-2-enyl]-3-methylbut-2-enyloxy}tetrahydro-2*H*-pyran (X). Yield 3.39 g (96%). IR spectrum, ν, cm^{-1}: 1655. ^{1}H NMR spectrum, δ, ppm: 1.45–1.59 m (4H), 1.62–1.90 m (8H), 2.14 d.d (0.5H, J_1 = 14, J_2 = 6 Hz), 2.19 d.d (0.5H, J_1 = 14, J_2 = 6 Hz), 2.31–2.40 m (1H), 2.51 t (1H, J = 7 Hz), 2.56 t (1H, J = 7 Hz), 3.41–3.49 m (1H), 3.60 t (1H, J = 7 Hz), 3.63 t (1H, J = 7 Hz), 3.81–3.89 m (1H), 4.39–4.46 m (0.5H), 4.50–4.58 m (1H), 4.66–4.69 m (0.5H), 4.85–4.97 m (2.5H), 5.17–5.22 m (0.5H).

Dehydrochlorination of compounds IX and X (*general procedure*). Tetrahydropyranyl derivative **IX** or **X**, 2.5 mmol, was added to a solution of 420 mg (7.5 mmol) of potassium hydroxide in 7 ml of ethanol,

and the mixture was heated for 10 h under reflux. The mixture was cooled, the solvent was distilled off under reduced pressure, and 20 ml of diethyl ether and 20 ml of water were added to the residue. The organic layer was separated, washed with water (20 ml) and a saturated aqueous solution of NaCl (20 ml), dried over $MgSO_4$, and evaporated, and the residue was passed through a layer of silica gel (5 g), followed by washing with a 1:5 mixture of diethyl ether and petroleum ether. The solvent was distilled off from the eluate to obtain compound **XI** or **XII** as an equimolar mixture of diastereoisomers.

2-(1-Isobutyl-3-methylidenepent-4-enyloxy)-tetrahydro-2*H*-pyran (XI). Yield 0.56 g (95%). IR spectrum, ν, cm^{-1}: 1620. ^1H NMR spectrum, δ, ppm: 0.84 d (1.5H, J = 7 Hz), 0.88 d (3H, J = 7 Hz), 0.91 d (1.5H, J = 7 Hz), 1.21–1.31 m (1H), 1.36 d.d.d (0.5H, J_1 = 14, J_2 = 8, J_3 = 5 Hz), 1.43–1.61 m (4.5H), 1.63–1.89 m (3H), 2.23–2.34 m (1H), 2.47 d.d (0.5H, J_1 = 14, J_2 = 7 Hz), 2.79 d.d (0.5H, J_1 = 14, J_2 = 5 Hz), 3.43–3.51 m (1H), 3.76–3.84 m (0.5H), 3.86–3.98 m (1.5H), 4.63–4.67 m (1H), 5.03–5.10 m (3H), 5.24 d (0.5H, J = 17 Hz), 5.36 d (0.5H, J = 17 Hz), 6.34 d.d (0.5H, J_1 = 17, J_2 = 11 Hz), 6.35 d.d (0.5H, J_1 = 17, J_2 = 11 Hz). Found, %: C 75.35; H 11.23. $C_{15}H_{26}O_2$. Calculated, %: C 75.58; H 10.99.

2-[3-Methylidene-1-(2-methylprop-1-enyl)pent-4-enyloxy]tetrahydro-2*H*-pyrane (XII). Yield 0.53 g (90%). IR spectrum, ν, cm^{-1}: 1625. ^1H NMR spectrum, δ, ppm: 1.44–1.59 m (4H), 1.62–1.73 m (7H), 1.74–1.88 m (1H), 2.24–2.36 m (1H), 2.52–2.63 m (1H), 3.39–3.47 m (1H), 3.81–3.89 m (1H), 4.48–4.68 m (2H), 4.92–4.98 m (0.5H), 5.01–5.09 m (3H), 5.17–5.22 m (0.5H), 5.26 d (0.5H, J = 17 Hz), 5.29 d (0.5H, J = 17 Hz), 6.34 d.d (0.5H, J_1 = 17, J_2 = 11 Hz), 6.38 d.d (0.5H, J_1 = 17, J_2 = 11 Hz). Found, %: C 76.04; H 10.33. $C_{15}H_{24}O_2$. Calculated, %: C 76.23; H 10.24.

2-Methyl-6-methylideneoct-7-en-4-ol (ipsenol) (I). Compound **XI**, 0.56 g (2.35 mmol), was dissolved in 6 ml of ethanol, 60 mg (0.235 mmol) of pyridinium *p*-toluenesulfonate was added, and the mixture was heated for 1 h under reflux until the initial compound disappeared completely (TLC). The mixture was diluted with water and extracted with diethyl ether (3×10 ml), the extracts were combined, washed with a saturated solution of $NaHCO_3$ (10 ml), water (10 ml), and an aqueous solution of NaCl (10 ml), and dried over $MgSO_4$, and the solvent was distilled off under reduced pressure. The residue was subjected to column chromatography on silica gel using petroleum ether–diethyl ether (7:1) as eluent. Yield 0.22 g (63%), colorless oily liquid. The spectral parameters of the product were consistent with those given in [15].

Esterification of compound VII (*general procedure*). Homoallyl alcohol **VII**, 2.74 g (14.5 mmol), was dissolved in 11.8 ml of anhydrous pyridine, the solution was cooled on an ice bath, and 30 mmol of benzoyl, isobutyryl, or pivaloyl chloride was added dropwise. The mixture was stirred for 2 h on cooling, 5 ml of water was added, and the mixture was stirred for 1–2 h at room temperature, diluted with 50 ml of water, and extracted with diethyl ether (2×30 ml). The combined extracts were washed with 10% aqueous sulfuric acid (2×40 ml) and saturated aqueous solutions of $NaHCO_3$ (20 ml) and NaCl (20 ml) and dried over $MgSO_4$. The solvent was distilled off under reduced pressure to obtain ester **XII**–**XIV** as a yellowish oily liquid which was brought into the next step without additional purification.

1-[2-(2-Chloroethyl)prop-2-enyl]-3-methylbut-2-enyl benzoate (XII). Yield 4.07 g (96%). IR spectrum: ν 1720 cm^{-1}. ^1H NMR spectrum, δ, ppm: 1.73–1.75 m (3H), 1.79–1.81 m (3H), 2.36 d.d (1H, J_1 = 14, J_2 = 6 Hz), 2.52–2.60 m (3H), 3.63 t (2H, J = 7 Hz), 4.89–4.91 m (1H), 4.97 s (1H), 5.21–5.26 m (1H), 5.82–5.92 m (1H), 7.39–7.46 m (2H), 7.50–7.57 m (1H), 8.02 d (2H). ^{13}C NMR spectrum, δ_C, ppm: 18.48, 25.64, 38.96, 41.39, 42.41, 70.25, 115.14, 123.16, 128.18, 129.44, 130.55, 132.64, 137.71, 141.13, 165.71.

1-[2-(2-Chloroethyl)prop-2-enyl]-3-methylbut-2-enyl 2-methylpropanoate (XIII). Yield 3.56 g (95%). IR spectrum: ν 1740 cm^{-1}. ^1H NMR spectrum, δ, ppm: 1.12 d (3H, J = 7 Hz), 1.13 d (3H, J = 7 Hz), 1.71 s (3H), 1.72 s (3H), 2.22 d.d (1H, J_1 = 14, J_2 = 6 Hz), 2.38 d.d (1H, J_1 = 14, J_2 = 8 Hz), 2.44–2.54 m (3H), 3.61 t (2H, J = 7 Hz), 4.87–4.89 m (1H), 4.91 s (1H), 5.08–5.13 m (1H), 5.56–5.63 m (1H). ^{13}C NMR spectrum, δ_C, ppm: 18.39, 18.83, 18.98, 25.59, 34.06, 38.89, 41.37, 42.41, 69.13, 114.89, 123.30, 137.31, 141.25, 176.27.

1-[2-(2-Chloroethyl)prop-2-enyl]-3-methylbut-2-enyl 2,2-dimethylpropanoate (XIV). Yield 3.68 g (93%). IR spectrum, ν, cm^{-1}: 1735. ^1H NMR spectrum, δ, ppm: 1.15 s (9H), 1.71 s (3H), 1.72 s (3H), 2.22 d.d (1H, J_1 = 14, J_2 = 6 Hz), 2.38 d.d (1H, J_1 = 14, J_2 = 8 Hz), 2.51 t (2H, J = 7 Hz), 3.61 t (2H, J = 7 Hz), 4.87–4.89 m (1H), 4.91 s (1H), 5.06–5.11 m (1H), 5.53–5.59 m (1H). ^{13}C NMR spectrum, δ_C, ppm: 18.36, 25.58, 27.07, 38.62, 38.82, 41.35, 42.40, 69.15, 114.85, 123.33, 137.02, 141.25, 177.62.

2-Methyl-6-methylideneocta-2,7-dien-4-ol (ipsdienol) (II). Ester **XII**, **XIII**, or **XIV**, 12.8 mmol, was added in one portion at room temperature to a solution of *t*-BuOK prepared from 1.25 g (32 mmol) of metallic potassium and 30 ml of *tert*-butyl alcohol. The mixture was heated for 2.5 h under reflux, 10 ml of water was added, and *tert*-butyl alcohol was distilled off under atmospheric pressure. The residue was diluted with 20 ml of ethanol, 2.0 g (36 mmol) of potassium hydroxide was added, and the mixture was heated under reflux for 1 h (esters **XII** and **XIII**) or 5 h (**XIV**). Most part of the solvent was distilled off under atmospheric pressure, 40 ml of water was added to the residue, and the product was extracted into diethyl ether (2×20 ml). The extracts were washed with water (10 ml) and saturated aqueous solutions of $NaHCO_3$ (10 ml) and NaCl (20 ml) and dried over $MgSO_4$. The solvent was distilled off under reduced pressure, and the residue was purified by column chromatography on silica gel using petroleum ether–diethyl ether as eluent. The yield of ipsdienol **II** was 63, 76, or 81% from ester **XII**, **XIII**, or **XIV**, respectively. Its spectral parameters were in agreement with published data [15].

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