Facile synthesis of (±)-2,6-dimethyloctan-1-ol formate, the biologically active analog of the smaller flour beetle aggregation pheromone, from 1-allyloxy- and 1-benzyloxy-2,6-dimethyl-2,7-octadienes, the telomers of isoprene with allyl and benzyl alcohols

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A careful investigation of the telomerization of isoprene with allyl, benzyl, 2-chloroethyl and methyl alcohols on π-allylpalladium complex catalysts was carried out. The structures of the obtained telomers were determined by ^{1}H NMR spectroscopy. 1-Alkoxy-2,6-dimethyl-2,7-octadiene is a predominant telomer. 2,6-Dimethyloctan-1-ol, which reacts with HCOOH to give (±)-2,6-dimethyloctan-1-ol formate in high yield, was obtained from 1-allyloxy- and 1-benzyloxy-2,6-dimethyl-2,7-octadienes by the removal of allyl and benzyl protective groups and by the hydrogenation of double bonds.

Key words: isoprene; allyl alcohol, benzyl alcohol; telomerization; π-allylpalladium catalysts; 1-alkoxy-2,6-dimethyl-2,7-octadienes; 1-hydroxy-2,6-dimethyloctane, (±)-2,6-dimethyloctan-1-ol formate, pheromone.

(±)-2,6-Dimethyloctan-1-ol formate (**1**) is a biologically active isostere of 4,8-dimethyldecanal, the aggregation pheromone of the beetle *Fribolium confusum*.[1] The described syntheses[1–4] of this attractant are rather complicated.

In this work we used the telomerization of isoprene with allyl, benzyl, and 2-chloroethyl alcohols to obtain 1-allyloxy-, 1-benzyloxy-, and 1-(2-chloroethoxy)-2,6-dimethyl-2,7-octadienes, which contain the allyl, benzyl, or 2-chloroethyl groups that are widely used in synthetic organic chemistry as readily cleavable protective groups for alcohols. Deprotection of the OH groups protected with these moieties and hydrogenation of the double bonds should readily lead to 2,6-dimethyloctan-1-ol (**2**), and its esterification with formic acid[1] easily gives the target formate **1**.

It was established,[5,6] that the two isomeric telomers are formed when the telomerization of isoprene with alcohols on complex palladium catalysts proceeds: 1-alkoxy-2,6-dimethyl-2,7-octadiene ("head to tail") and 1-alkoxy-2,7-dimethyl-2,7-octadiene ("tail to tail"), the former is obtained in a predominant amount.

However, the detailed analysis of literature data concerning the telomerization of isoprene with alcohols on palladium catalysts showed their discrepancy even when the same palladium catalysts and reaction conditions were used. It was shown[7–10] that the telomerization of isoprene with methanol results in two isomeric telomers: 1-methoxy-2,6-dimethyl-2,7-octadiene (**3**) in a predominant amount and 1-methoxy-2,7-dimethyl-2,7-octadiene (**4**) in a lesser amount. According to other data[11,12] not telomer **4**, but telomer **3** and 1-methoxy-3,6-dimethyl-2,7-octadiene ("tail to head") are reaction products. It was also supposed,[13] that 3-methoxy-2,7-dimethyl-1,7-octadiene rather than telomer **3** is obtained along with telomer **4**. Four isomeric telomers were obtained[14] by the telomerization of isoprene with methanol: 1-methoxy-3,6-dimethyl-1,7-octadiene, 3-methoxy-2,6-dimethyl-1,7-octadiene, telomers **3** and **4**, but no data confirming the structures of these telomers were presented. Two isomeric telomers are formed by the telomerization of isoprene with ethanol, *n*-propanol and butanol:[8–12] 1-alkoxy-2,6-dimethyl-2,7-octadienes and 1-alkoxy-2,7-dimethyl-2,7-octadienes. Four telomers in which isoprene molecules are connected "tail to tail" and "tail to head" were obtained[15] by the telomerization of isoprene with 2,2,2-trifluoroethanol, whereas three isomeric telomers in which isoprene molecules are connected only "tail to tail" are formed by the telomerization with benzyl alcohol: 1-benzyloxy-2,7-dimethyl-2*E*,7-octadiene, 1-benzyloxy-2,7-dimethyl-2*Z*,7-octadiene and 3-benzyloxy-2,7-dimethyl-1,7-octadiene. Three telomers were obtained by the similar procedure with furfuryl alcohol.

Taking into account the mentioned discrepancy of the data concerning the telomerization of isoprene with alcohols, we studied in detail the telomerization of isoprene with methanol under the action of the known[7] catalytic system $(\pi\text{-AllPdCl})_2$ + Ph_3P + MeONa in benzene according to earlier described procedure.[12] This system allows to carry out the telomerization of isoprene

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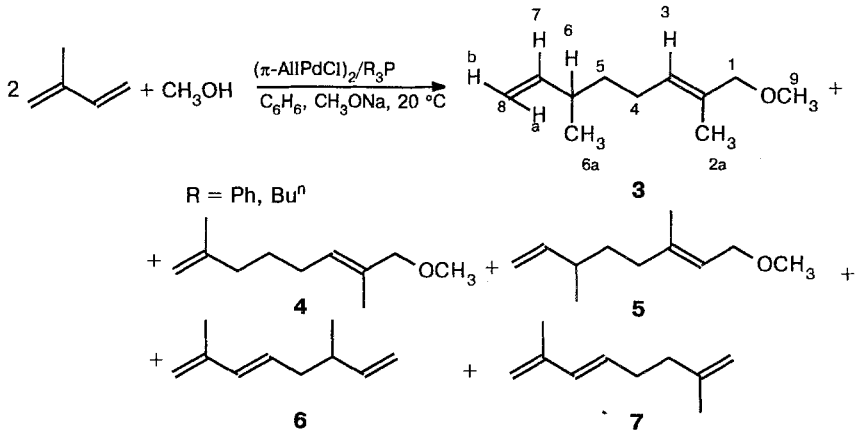
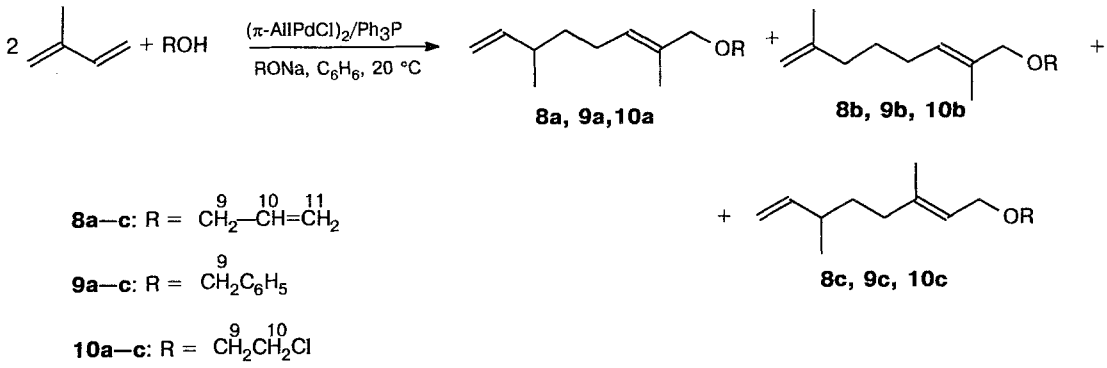
Scheme 1



Scheme 2



with alcohols at 20 °C, and due to this fact the possibility of secondary reactions with telomers is excluded almost completely, which, as it has been noted, take place when the telomerization proceeds at higher temperatures.[7,14]

We established that three isomeric telomers (telomer **3**, telomer **4**, and 1-methoxy-3,6-dimethyl-2,7-octadiene (**5**)) and in minor amount two isomeric dimers of isoprene, **6** and **7** (Scheme 1) are formed by the telomerization of isoprene with methanol under the action of the catalytic system $(\pi\text{-AllPdCl})_2$ + R_3P + MeONa, where R is Bu^n, Ph, at 20 °C.

The yield and ratio of telomers **3**, **4**, and **5** depend on factors such as the amount of inert solvent (benzene) relative to CH_3OH, the nature of the phosphine, the ratio of isoprene to CH_3OH, and the Pd/P and Pd/CH_3ONa ratios. The yield of telomer mixture is 90—92 %, and the yield of telomer **3** is 70—75 %, which correlates with literature data.[6,12] The structures of telomers **3**—**5** were confirmed by ^1H NMR spectroscopy. The presence of the three isomeric telomers was determined unambigously by capillary GLC. The statement[6,13] that only two isomeric telomers are formed by the telomerization of isoprene with methanol and with other primary alcohols is apparently connected with the fact that the GLC analysis was carried out on a column unsuitable for separating telomers **4** and **5**, and insufficiently powerful NMR spectrometers were used for the determination of the structure of the isomeric telomers.

We demonstrated that the telomerization of isoprene with allyl and benzyl alcohols proceeds smoothly under the action of the catalytic system $(\pi\text{-AllPdCl})_2$ + Ph_3P + RONa (Scheme 2).

A mixture of three isomeric telomers is thereby obtained in high yield: 1-alkoxy-2,6-dimethyl-2,7-octadienes (**8a** and **9a**), 1-alkoxy-2,7-dimethyl-2,7-octadienes (**8b** and **9b**), and 1-alkoxy-3,6-dimethyl-2,7-octadienes (**8c** and **9c**). The telomerization of isoprene with chloroethanol proceeds in low yield, resulting in the same three isomeric telomers **10a**—**10c**. The composition of the telomerization mixtures is given in Table 1. Telomers **8a**, **9a**, and **10a** were isolated as pure substances by vacuum distillation on an efficient column. The structures of telomers **8a**—**8c**, **9a**—**9c**, and **10a**—**10c** were confirmed by ^1H NMR spectroscopy data.

The transformation of telomer **8a** into alcohol **2** was carried out by Scheme 3.

Propenyl ether (**11**) was formed by the isomerization of **8a** allyl group under the action of homogeneous catalysts $(PhCN)_2PdCl_2$[16] or $3,3\text{-}(Ph_3P)_2\text{-}3H\text{-}3,1,2\text{-}RhC_2B_9H_{11}$,[17] which was hydrolyzed in water—alcohol

Scheme 3

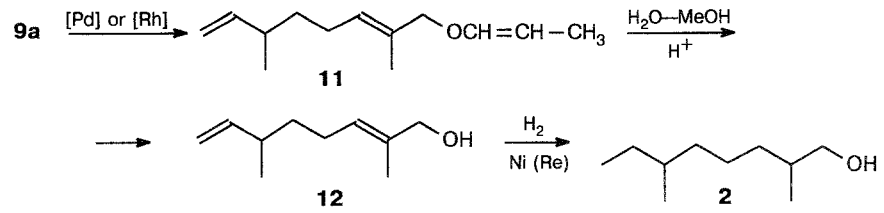
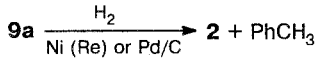


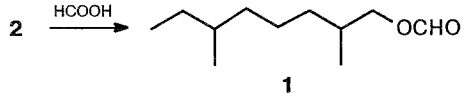
Table 1. Composition and yield of a mixture of telomers with methyl (**3—5**), allyl (**8a—8c**), benzyl (**9a—9c**), and chloroethyl (**10a—10c**) alcohols

Starting alcohol	Yield (%)	Percentages of telomers in a mixture
MeOH	81.0	**3** : **4** : **5** = 67.0 : 18.0 : 15.0
CH_2=CH–CH_2OH	70.0	**8a** : **8b** : **8c** = 76.0 : 17.0 : 7.0
$PhCH_2OH$	70.0	**9a** : **9b** : **9c** = 78.0 : 19.0 : 3.0
$ClCH_2CH_2OH$	38.0	**10a** : **10b** : **10c** = 62.0 : 8.0 : 30.0

medium in the presence of acid to give 2,6-dimethyloctadienol (**12**). The latter was hydrogenated over Raney nickel to give alcohol **2**. Alcohol **2** was also obtained from telomer **9a**.



Hydrogenation[18] of compound **9a** in acetic acid over Pd/C with hydrogen pressure of 2—4 atm gives compound **2** in high yield, whereas hydrogenation under drastic conditions results, together with hydrogenolysis of benzyl group, in hydrogenation of benzene ring with the formation of 1-cyclohexylmethyloxy-2,6-dimethyloctane. 2,6-Dimethyloctan-1-ol formate (**1**) is formed by the esterification of alcohol **2** with formic acid according to the known procedure.[1]



It was found that the reaction of telomer **10a** with magnesium in ether or THF proceeds very slowly, and the yield of alcohol **12** is low. It was indicated earlier[5,8,15] that higher primary alcohols have low reactivity in the telomerization with isoprene on palladium catalysts and, therefore, telomers are formed in low yield or are not formed at all, and dimerization of isoprene into isomeric dimethyloctatrienes becomes the main reaction.

However, we found in this work that higher alcohols such as *n*-amyl and *n*-nonyl alcohols in benzene solution when using the catalytic system (π-AllPdCl)$_2$ + Ph_3P + RONa are involved in telomerization with isoprene, resulting, in moderate yield, in a mixture of isomeric dimethyloctadienylamyl and dimethyloctadienylnonyl esters, respectively.

Experimental

GLC analysis was carried out on an LKhM-8MD chromatograph in a helium stream on 2 m × 4 mm columns with 15 % SKTFT-50kh on Chromaton N-AW-HMDS, with 5 % neopentylglycolsuccinate on Chromosorb G, with 5 % silicone SE-30 on Chromaton N-AW, on a quartz capillary column (l = 25 m) and with SE-54 (helium was the carrier gas, 1.3 atm). ^{1}H NMR spectra were recorded in deuterobenzene with a Bruker WP-200-SY instrument. All telomerization experiments were carried out in an argon atmosphere using anhydrous alcohols and benzene; freshly distilled dry isoprene was used.

General procedure of the telomerization of isoprene with alcohols. Solutions of 4.3 mmol of PPh_3 in 10 mL of benzene and 0.89 mol of isoprene in 80 mL of benzene were added to a solution of 2.2 mmol of (π-AllPdCl)$_2$ in 20 mL of benzene; that was followed by the addition of a sodium alkoxide solution prepared from 12.9 mmol of sodium in 15 mL of a primary alcohol. While the mixture was stirring, 1.32 mol of a primary alcohol was added. Since the telomerization reaction is exothermic, the reaction temperature was kept within 15—20 °C by cooling with ice water. Solid sodium methoxide (5 mmol) was used as a base in the telomerization of isoprene with 2-chloroethanol. Then the reaction solution was allowed to stand at 20 °C for 48—72 h. 100 mL of water was then added, and an organic layer was separated, washed with 50 mL of water, and dried over Na_2SO_4. After benzene and alcohol were removed *in vacuo* (100—120 Torr), the residue was distilled from the flask using a dephlegmator to separate dimers of isoprene from telomers. Ratios of isomers were measured by GLC and ^{1}H NMR spectroscopy. Composition and yield data for telomer mixtures **3—5**, **8a—8c**, **9a—9c**, and **10a—10c** are given in Table 1. Telomers **3**, **8a**, **9a**, and **10a** were isolated as pure substances by fractional distillation on a rectifying column. Complete assignments of the ^{1}H NMR spectra are given for these compounds. All other isomeric telomers were not isolated as pure substances, and their ^{1}H NMR spectra were registered in mixtures of isomeric telomers. Data on individual telomers **3**, **8a**, **9a**, and **10a** are summarized in Table 2.

1-Methoxy-2,6-dimethyl-2,7-octadiene (3). ^{1}H NMR (C_6D_6, δ): 5.20 (ddd, 1 H, H(8a), $^3J_{8a-7}$ = 17.4 Hz, $^2J_{8a-8b}$ = 2.1 Hz, $^4J_{8a-6}$ = 1.2 Hz); 4.81 (ddd, 1 H, H(8b), $^3J_{8b-7}$ = 10.2 Hz, $^4J_{8b-7}$ = 0.5 Hz); 5.675 (ddd, 1 H, H(7), $^3J_{7-6}$ = 6.9 Hz); 2.117 (m, 1 H, CH(6), $^3J_{6-6a}$ = 6.8 Hz); 0.966 (d, 3 H, $CH(6)_3$); 1.328 (dt, 2 H, $CH(5)_2$, $^3J_{5-4}$ = 7.4 Hz); 2.017 (dt, 2 H, $CH(4)_2$, $^3J_{4-3}$ = 7.4 Hz); 5.378 (m, 1 H, H(3), $^4J_{3-2a}$ = 1.3 Hz, $^4J_{3-1}$ = 1.3 Hz); 1.645 (s, 3 H, $CH(2a)_3$); 3.753 (s, 2 H, $CH(1)_2$); 3.162 (s, 3 H, $CH(9)_3$).

Table 2. Physicochemical data for 1-alkoxy-2,6-dimethyl-2,7-octadienes

Telomer	B.p./°C (*p*/Torr)	n_D^{20}	Found / Calculated (%)		Molecular formula
			C	H	
3	76—78 (7)	1.4540	78.46 78.57	11.78 11.90	$C_{11}H_{20}O$
8a	102—103 (9)	1.4590	79.81 80.40	11.03 11.34	$C_{13}H_{22}O$
9a	123—125 (2)	1.5070	83.63 80.60	9.79 9.83	$C_{17}H_{24}O$
10a*	108—110 (3)	1.4738	66.35 66.51	9.78 9.69	$C_{12}H_{21}C_{10}$

* Found (%): Cl, 16.39. Calculated (%): Cl, 16.49.

1-Methoxy-2,7-dimethyl-2,7-octadiene (4). ^{1}H NMR (C_6D_6, δ): 4.763 (m, 2 H, H(8a) and H(8b)); 1.682 (s, 3 H, $CH(7a)_3$); 1.931 (t, 2 H, $CH(6)_2$); 1.452 (m, 2 H, $CH(5)_2$); 1.969 (m, 2 H, $CH(4)_2$); 5.281 (m, 1 H, CH(3)); 1.571 (s, 3 H, $CH(2a)_3$); 3.662 (s, 2 H, $CH(1)_2$); 3.14 (s, 3 H, $CH(9)_3$).

1-Methoxy-3,6-dimethyl-2,7-octadiene (5). ^{1}H NMR (C_6D_6, δ): 5.610 (ddd, 1 H, H(7), $^3J_{8a-7}$ = 17.4 Hz, $^3J_{8b-7}$ = 10.2 Hz, $^3J_{7-6}$ = 6.9 Hz); 3.889 (d, 2 H, $H(1)_2$, J_{2-1} = 9.5 Hz); 3.222 (s, 3 H, $CH(9)_3$).

1-Allyloxy-2,6-dimethyl-2,7-octadiene (8a). ^{1}H NMR (C_6D_6, δ): 4.986 (ddd, 1 H, H(8a), $^3J_{8a-7}$ = 17.7 Hz, $^2J_{8a-8b}$ = 1.1 Hz); 4.968 (ddd, 1 H, H(8b), $^3J_{8b-7}$ = 10.5 Hz, $^4J_{8b-6}$ = 1.1 Hz); 5.672 (ddd, 1 H, H(7), J_{7-6} = 7.5 Hz); 2.143 (m, 1 H, CH(6), $^3J_{6-6a}$ = 6.7 Hz, $^3J_{6-5}$ = 6.9 Hz); 0.992 (d, 3 H, $CH(6a)_3$, $^3J_{6-6a}$ = 6.7 Hz); 1.343 (dt, 2 H, $CH(5)_2$, $^3J_{5-4}$ = 6.9 Hz); 2.042 (dt, 2 H, $CH(4)_2$, $^3J_{4-5}$ = 7.2 Hz); 5.417 (m, 1 H, H(3), $^3J_{4-3}$ = 7.2 Hz, $^4J_{3-2a}$ = 1.4 Hz, $^4J_{3-1}$ = 1.4 Hz); 1.659 (s, 3 H, $CH(2a)_3$); 3.829 (s, 2 H, $CH(1)_2$); 3.863 (dt, 2 H, $CH(9)_2$, $^3J_{9-10}$ = 4.8 Hz, $^4J_{9-11a}$ = 1.7 Hz, $^4J_{9-11b}$ = 1.7 Hz); 5.903 (ddt, 1 H, H(10), $^3J_{10-11a}$ = 17.3 Hz, $^3J_{10-11b}$ = 10.4 Hz, $^3J_{9-10}$ = 4.8 Hz); 5.283 (ddt, 1 H, H(11a), $^2J_{11a-11b}$ = 1.9 Hz); 5.103 (1 H, H(11b)).

1-Allyloxy-2,7-dimethyl-2,7-octadiene (8b). ^{1}H NMR (C_6D_6, δ): 4.771 (m, 2 H, H(8a) and H(8b)); 1.687 (s, 3 H, $CH(7a)_3$); 1.659 (s, 3 H, $CH(2a)_3$).

1-Allyloxy-3,6-dimethyl-2,7-octadiene (8c). ^{1}H NMR (C_6D_6, δ): 5.661 (ddd, 1 H, H(7), $^3J_{8a-7}$ = 17.7 Hz, $^3J_{8b-7}$ = 10.5 Hz, $^3J_{7-6}$ = 7.5 Hz); 0.991 (d, 3 H, $CH(6a)_3$, $^3J_{6-6a}$ = 6.7 Hz).

1-Benzyloxy-2,6-dimethyl-2,7-octadiene (9a). ^{1}H NMR (C_6D_6, δ): 4.976 (dd, 1 H, H(8a), $^3J_{8a-7}$ = 17.0 Hz, $^2J_{8a-8b}$ = 1.5 Hz); 4.970 (dd, 1 H, H(8b), $^3J_{8b-7}$ = 10.4 Hz); 5.653 (ddd, 1 H, H(7), $^3J_{7-6}$ = 7.7 Hz); 0.970 (d, 3 H, $CH(3)_3$); 1.371 (m, 1 H, CH(6), $^3J_{6-6a}$ = 6.7 Hz, $^3J_{6-5}$ = 7.8 Hz); 1.318 (dt, 2 H, $CH(5)_2$, $^3J_{5-4}$ = 7.1 Hz); 2.033 (dt, 2 H, $CH(4)_2$, $^3J_{4-3}$ = 7.1 Hz); 5.408 (tm, 1 H, H(3), $^4J_{3-2a}$ = 1.3 Hz, $^4J_{3-1}$ = 1.3 Hz); 1.664 (s, 3 H, $CH(2a)_3$); 3.845 (s, 2 H, $CH(1)_2$); 4.371 (s, 2 H, $CH(9)_2$); 7.13—7.34 (m, 5 H, Ph).

1-Benzyloxy-2,7-dimethyl-2,7-octadiene (9b). ^{1}H NMR (C_6D_6, δ): 4.768 (m, 2 H, H(8a) and H(8b)); 1.678 (s, 3 H, $CH(7a)_3$); 1.621 (s, 3 H, $CH(2a)_3$); 7.282 (m, 5 H, Ph).

1-Benzyloxy-3,6-dimethyl-2,7-octadiene (9c). ^{1}H NMR (C_6D_6, δ): 5.635 (ddd, 1 H, H(7), $^3J_{8a-7}$ = 17.0 Hz, $^3J_{8b-7}$ = 10.4 Hz, $^3J_{7-6}$ = 7.6 Hz); 0.970 (d, 3 H, $CH(6a)_3$, $^3J_{6-6a}$ = 6.7 Hz).

1-(2-Chloroethoxy)-2,6-dimethyl-2,7-octadiene (10a). ^{1}H NMR (C_6D_6, δ): 4.955 (dd, 1 H, H(8a), $^3J_{8a-7}$ = 17.7 Hz, $^2J_{8a-8b}$ = 2.1 Hz); 4.911 (dd, 1 H, H(8b), $^3J_{8b-7}$ = 10.3 Hz); 5.650 (d, 1 H, H(7), $^3J_{7-6}$ = 7.9 Hz); 2.075 (m, 1 H, CH(6), $^3J_{6-6a}$ = 6.7 Hz, $^3J_{6-5}$ = 6.7 Hz); 0.973 (d, 3 H, $CH(6)_3$); 1.318 (dt, 2 H, $CH(5)_2$, $^3J_{5-4}$ = 6.7 Hz); 1.983 (dt, 2 H, $CH(4)_2$, $^3J_{4-3}$ = 6.7 Hz); 5.347 (tm, 1 H, H(3), $^4J_{3-2}$ = 1.4 Hz, $^4J_{3-1}$ = 1.4 Hz); 1.603 (dm, 3 H, $CH(2a)_3$); 3.785 (s, 2 H, $CH(1)_2$); 3.444 (s, 4 H, $CH(9)_2$ and $CH(10)_2$).

1-(2-Chloroethoxy)-2,7-dimethyl-2,7-octadiene (10b). ^{1}H NMR (C_6D_6, δ): 4.719 (m, 2 H, H(8a) and H(8b)); 3.950 (s, 2 H, $CH(1)_2$); 1.734 (dt, 3 H, $CH(7)_3$, $^4J_{3-2}$ = 1.3 Hz, $^4J_{2-1}$ = 1.3 Hz); 1.673 (dt, 3 H, $CH(2a)_3$, $^4J_{8a-7}$ = 1.2 Hz, $^4J_{8b-7}$ = 1.2 Hz, $^4J_{7-6}$ = 1.2 Hz).

1-(2-Chloroethoxy)-3,6-dimethyl-2,7-octadiene (10c). ^{1}H NMR (C_6D_6, δ): 4.957 (dd, 1 H, H(8a), $^3J_{8a-7}$ = 17.6 Hz, $^2J_{8a-8b}$ = 2.1 Hz); 4.952 (d, 1 H, H(8b), $^3J_{8b-7}$ = 9.8 Hz); 5.641 (d, 1 H, H(7), $^3J_{7-6}$ = 7.7 Hz); 0.983 (d, 3 H, $CH(6a)_3$, $^3J_{6-6a}$ = 6.9 Hz); 1.569 (s, 3 H, $CH(3)_3$); 3.916 (s, 1 H, $CH(1)_2$). The parameters of the ^{1}H NMR spectra for compounds **4**, **5b**, **8b**, **8c**, **9b**, **9c**, and **10b**, **10c** were established with a lower accuracy than for **3**, **8a**, **9a**, and **10a**, since the former were mixtures of compounds.

2,6-Dimethyl-2,7-octadiene-1-ol (12). *A.* A mixture of 5 g (25.6 mmol) of compound **8a** and 0.07 g of $(Ph_3P)_2RhHC_2B_9H_{11}$ was boiled in 5 mL of dry benzene for 16 h. After the benzene was removed, the residue was distilled, and 4.6 g of 2,6-dimethyl-2,7-octadiene (**11**) were obtained, b.p. 96—97 °C (5 Torr), n_D^{20} 1.4660.

B. The reaction in the presence of 0.1 g of $(PhCN)_2PdCl_2$ in abs. THF (60 °C, 8 h) was carried out similarly to *A*. The product **11** had n_D^{20} 1.4672 after distillation.

C. A solution of 4.5 g (23 mmol) of compound **11** in 11 mL of ethanol, 4 mL of water and 0.1 mL of conc. HCl was allowed to stand at 20 °C for 14 h. Then, it was poured into 15 mL of water, and twice extracted with ether. The ether extracts were washed with a $NaHCO_3$ solution and dried over Na_2SO_4. After ether was removed, 3.27 g (91.7 %) of alcohol **12** were obtained, b.p. 99—101 °C (16 Torr), n_D^{20} 1.4670, IR (ν/cm^{-1}): 3400 (OH). Found (%): C, 77.74; H, 11.74. $C_{10}H_{18}O$. Calculated (%): C, 77.92; H, 11.68.

2,6-Dimethyloctan-1-ol (2). *A.* A solution of 13 g (84mmol) of alcohol **12** in 60 mL of EtOH was hydrogenated over 3 g of Raney Ni (hydrogen pressure was 60 atm, 50 °C) for 6 h. The catalyst was filtered off, EtOH was removed, and the residue was distilled. 12.6 g (94.4 %) of alcohol **2** were obtained, b.p. 77—78 °C (1 Torr), n_D^{20} 1.4325 (*cf.* Ref. 14: n_D^{20} 1.4315).

B. A mixture of 23 g (89.8 mmol) of 1-benzyloxy-2,6-dimethyl-2,7-octadiene (**9a**) in 50 mL of MeCOOH and 1 g of Pd/C was hydrogenated at 20 °C and at hydrogen pressure of 4 atm as long as hydrogen absorption took place. The catalyst was filtered off, the solvent was removed *in vacuo*, water was added to the residue, and the latter was extracted with ether. The ether solution was washed with a $NaHCO_3$ solution and dried over Na_2SO_4. After the solvent being removed, the rest was distilled. 13.5 g (91 %) of alcohol **2** were obtained, b.p. 96 °C (7 Torr), n_D^{20} 1.4325. Found (%): C, 75.78; H, 13.93. $C_{10}H_{22}O$. Calculated (%): C, 75.94; H, 13.92.

C. A solution of 23 g (89.8 mmol) of compound **9a** in 70 mL of EtOH was hydrogenated in the presence of 5 g of Raney Ni (hydrogen pressure was 120 atm, 160 °C) for 8 h. After the usual treatment the residue was distilled. 5 g of alcohol **2** were obtained, b.p. 96 °C (7 Torr), n_D^{20} 1.4325,

and 9.7 g of 1-cyclohexylmethyloxy-2,6-dimethyloctane were obtained, b.p. 160 °C (5 Torr), n_D^{20} 1.4770. Found (%): C, 81.16; H, 12.62. $C_{13}H_{34}O$. Calculated (%): C, 80.36; H, 13.33. IR spectrum of the sample does not contain absorption bands of OH group and benzene ring.

A mixture of 4 g (25.3 mmol) of alcohol **2** and 2.6 g (25.3 mmol) of acetic anhydride with 0.1 mL of H_2SO_4 was heated at 100 °C for 2 h. After cooling the mixture was poured onto ice and extracted with ether, and the ether extracts were washed with a $NaHCO_3$ solution and dried over Na_2SO_4. Ether was removed, the residue was distilled, and 4.5 g (88.93 %) of **1-acetoxy-2,6-dimethyloctane** were obtained, b.p. 77—78 °C (1 Torr), n_D^{20} 1.4288. Found (%): C, 71.17; H, 11.88. $C_{12}H_{24}O_2$. Calculated (%): C, 72.00; H, 12.00.

2,6-Dimethyloctan-1-ol formate (1). A solution of 12 g of compound **2** in 60 mL of 98 % HCOOH was heated at 70 °C for 1 h. After cooling, it was poured onto ice and extracted with ether (3×30 mL). Combined extracts were washed with a $NaHCO_3$ solution and with water and dried over Na_2SO_4. The solvent was removed. 11.02 g (83.1 %) of compound **1** were obtained by distillation, b.p. 91—92 °C (14 Torr), n_D^{20} 1.4266 (*cf.* Ref. 1: n_D^{20} 1.4260).

Telomerization of isoprene with nonyl alcohol. A solution of sodium *n*-nonoxide, prepared from 0.1 g (4.3 mmol) of sodium and 50 mL of *n*-nonyl alcohol was added to a solution of 0.27 g (0.73 mmol) of $(AllPdCl)_2$, 0.38 g (1.4 mmol) of PPh_3, and 20 g (0.29 mol) of isoprene in 40 mL of benzene. The mixture was allowed to stand at 20 °C for 72 h. After the usual treatment 16.46 g (38 %) of a mixture of three isomeric *n*-nonyloxydimethyl-2,7-octadienes were obtained, b.p. 141—143 °C (1 Torr). Found (%): C, 81.10; H, 12.82. $C_{19}H_{36}O$. Calculated (%): C, 81.42; H, 12.85.

Telomerization of isoprene with *n*-amyl alcohol. The reaction was carried out following the procedure described above, by mixing 0.18 g (0.49 mmol) of $(AllPdCl)_2$, 0.25 g (0.9 mmol) of PPh_3, 40 mL of benzene, 13.6 g (0.2 mol) of isoprene, 0.06 g (2.58 mmol) of sodium, and 18 g (0.2 mol) of *n*-amyl alcohol. 9.57 g (42 %) of a mixture of three isomeric amyloxydimethyl-2,7-octadienes were obtained by distillation, b.p. 104—109 °C (2 Torr), n_D^{20} 1.4590. Found (%): C, 80.46; H, 12.36. $C_{15}H_{28}O$. Calculated (%): C, 80.35; H, 12.24.

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