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PALLADIUM-CATALYZED ASYMMETRIC TELOMERIZATION OF ISOPRENE. PREPARATION OF OPTICALLY ACTIVE CITRONELLOL

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Summary

Palladium-catalyzed asymmetric telomerization of isoprene with methanol in the presence of optically active phosphorus ligands gave 1-methoxy-2,6-dimethyl-2,7-octadiene ('head-to-tail' methoxy telomer I) in an optically active form. This methoxy telomer I is a very useful intermediate for the synthesis of (+)- or (—)-citronellol through three steps. Various menthylphosphorus derivatives were prepared as optically active phosphorus ligands and their steric effects on this asymmetric telomerization were investigated. The maximum optical yield (35%) was obtained when menthyldiisopropylphosphine was used.

Introduction

Asymmetric synthesis catalyzed by transition metal complexes has recently been investigated, especially in the fields of hydrogenation [1] and hydrosilylation [2]. But there are a few reports dealing with the asymmetric formation of a new carbon—carbon bond. Wilke et al. [3] and Kumada et al. [4] found the asymmetric cooligomerization of 1,3-cyclooctadiene with ethylene and the asymmetric cross coupling reaction of Grignard reagents with organic halides in the presence of nickel catalysts containing optically active phosphines, respectively. It is now well known that isoprene is telomerized with active hydrogen compounds such as alcohols [5] or amines [6] by using various transition metal complexes. Although it was expected that these telomers could provide very useful intermediates for terpenoid derivatives, the catalytic chemistry has not been able to supply many successful pathways, because it is very difficult to construct the desired 'head-to-tail' structure selectively. However, the reaction of diethylamine with isoprene catalyzed by butyllithium gives selectively 1-diethylamino-3,7-dimethyl-2,6-octadiene [8], which is converted to the

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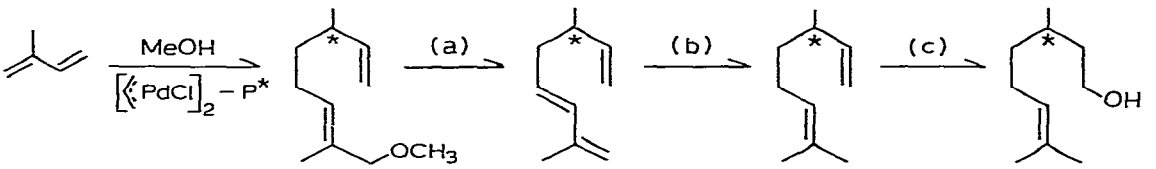
various monoterpenes by normal organic synthesis [9]. On the other hand, methanol can function as a telogen toward isoprene in the presence of a palladium catalyst and the desired 'head-to-tail' telomer is obtained [7]. In a preliminary communication [10], we reported the synthesis of (+)- or (—)-citronellol starting from isoprene (Scheme 1). The first step was the telomeri-

SCHEME 1



(a) $NiCl_2(PBu_3)_2$, NaOMe in iso-PrOH

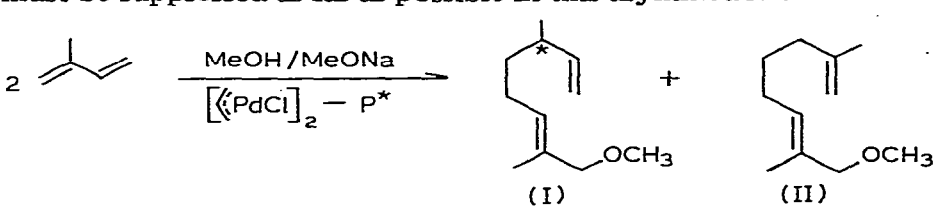
(b) $Cr(CO)_3(PhCOOCH_3)$ in Hexane (H_2 50 kg/cm^2)

(c) Hydroboration - Oxidation

zation of isoprene with methanol using tertiary phosphine-palladium complexes to yield 1-methoxy-2,6-dimethyl-2,7-octadiene (a 'head-to-tail' methoxy telomer I). In this telomerization, a catalyst containing an optically active phosphine gave the methoxy telomer I in an optically active form in moderate yield. We describe here the details of this asymmetric telomerization of isoprene with methanol by using palladium catalysts with optically active phosphines. Several kinds of optically active phosphines have been reported. However, typical bidentate ligands such as 2,3-O-isopropylidene-1,4-bis(diphenylphosphino)-2,3-butanediol (DIOP) showed very low activity in this telomerization. Therefore, we employed a series of monodentate phosphines with a menthyl substituent derived from (—)-*l*-menthol and investigated the effects on the conversion of isoprene, the selectivity of the 'head-to-tail' telomer I, and the optical yield.

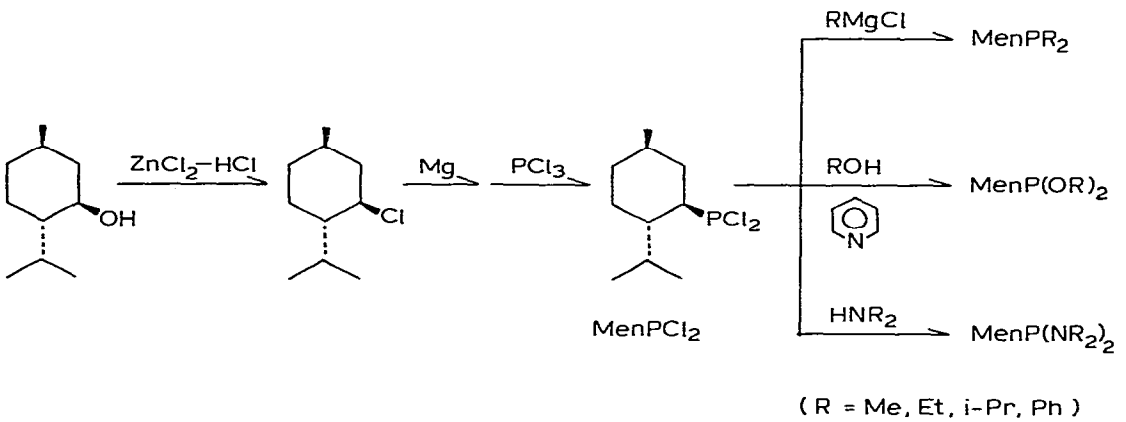
Results and discussion

Treatment of isoprene with methanol in the presence of a catalyst system comprising bis(π-allylpalladium chloride), triphenylphosphine, and sodium methoxide at room temperature gave ca. 100% conversion of isoprene mainly into 1-methoxy-2,6-dimethyl-2,7-octadiene ('head-to-tail' methoxy telomer I) after 48 hours. In this catalyst system, optically active phosphines were used in place of triphenylphosphine to obtain optically active methoxy telomer I. In this telomerization 1-methoxy-2,7-dimethyl-2,7-octadiene (a 'tail-to-tail' methoxy telomer II) is concomitantly obtained. Formation of this telomer II, which is a regioisomer of the telomer I and is not converted into citronellol, must be suppressed as far as possible in this asymmetric telomerization.



We have prepared a series of optically active phosphines containing a chiral menthyl group to investigate the regioselectivity and the optical yield in this telomerization reaction. The introduction of the menthyl group was carried out by treatment of phosphorus trichloride with the menthyl Grignard reagent [11]. This menthyldichlorophosphine was readily converted to menthyldialkylphosphines ($MenPR_2$), dialkyl menthylphosphonites ($MenP(OR)_2$), and bis(dialkylamino)menthylphosphines ($MenP(NR_2)_2$) by treatment with alkyl Grignard reagents, alcohols, and secondary amines, respectively (Scheme 2).

SCHEME 2



These menthylphosphorus derivatives show the specific rotations in the region of —60.1 to —122.3° except for diphenyl menthylphosphonite (—18.6°). The chirality of the telomer I obtained in this asymmetric telomerization was, however, not uniformly induced because the other two substituents on phosphorus were greatly different. Thus menthyldialkylphosphines ($MenPR_2$) and bis(dialkylamino)menthylphosphines ($MenP(NR_2)_2$) induced the same chirality and gave the (+)-telomer I preferentially, whereas dialkyl menthylphosphonites ($MenP(OR)_2$) produced the (—)-telomer I in preference to the (+)-telomer I (Table 1). For example, menthyldiisopropylphosphine ($MenP(C_3H_7\text{-iso})_2$) gave the (+)-telomer I in 35% optical yield (Run 3) and bis(dimethylamino)menthylphosphine ($MenP(NMe_2)_2$) in 11% optical yield (Run 9). On the other hand, dimethyl menthylphosphonite ($MenP(OMe)_2$) led to the formation of the (—)-telomer I in 8% optical yield (Run 5).

Dialkyl menthylphosphonites or bis(dialkylamino)menthylphosphines had a better regioselectivity for formation of the telomer I than menthyldialkylphosphines. For example, menthyldimethylphosphine gave the methoxy telomers I and II in a 44:56 ratio (Run 1) whereas the methoxy telomer I was obtained more selectively when dimethyl menthylphosphonite was used (I:II = 86:14) (Run 5). Furthermore, the conversion of isoprene was nearly 100% when dialkyl menthylphosphonites and bis(dialkylamino)menthylphosphine were employed. However, the optical yields of the (—)- or (+)-telomer I were relatively low, even when rather bulky bis(dimethylamino)menthylphosphine was used (Run 9). In the case of menthyldialkylphosphines, the steric bulk of the phosphines exhibited remarkable effects on both the conversion of isoprene

TABLE 1

ASYMMETRIC TELOMERIZATION OF ISOPRENE WITH METHANOL

Run	Phosphine $MenPR_2$	θ [a]	Conversion of isoprene (%)	Yield of telomers I and II (%)	Ratio of I to II	$[\alpha]_D^{15}$ of I	Optical yield (%)
1	$MenPMe_2$	118	65	45	44:56	+1.95	20
2	$MenPEt_2$	132	85	60	53:47	+0.95	10
3	$MenP(iso\text{-}Pr)_2$	160	38	14	63:37	+3.38	35
4	$MenPPh_2$	145	100	93	69:31	+2.78	29
5	$MenP(OMe)_2$	107	98	78	86:14	—0.73	8
6	$MenP(OEt)_2$	109	100	76	84:16	—0.77	8
7	$MenP(O\text{-}iso\text{-}Pr)_2$	130	100	55	85:15	—0.14	1
8	$MenP(OPh)_2$	128	94	60	84:16	—0.74	8
9	$MenP(NMe_2)_2$	157	100	72	83:17	+1.03	11
10	neo-$MenPPh_2$	—	91	58	79:21	—1.26	13

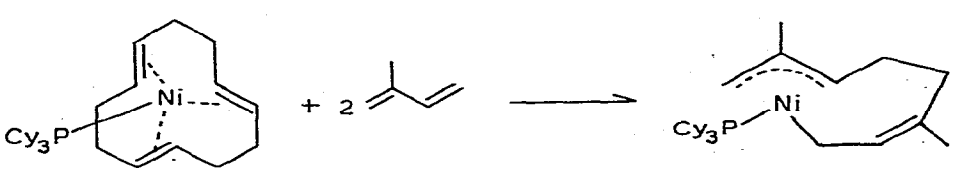
[a] θ is the cone angle of PR_3 defined by Tolman [20]. This value may give a measure of the steric parameter of the type $MenPR_2$.

and the optical yield of the (+)-telomer I. Thus the bulky menthyldiisopropylphosphine gave the best result with respect to the optical yield (35%), although the conversion of isoprene was lowered to 38% (Run 3).

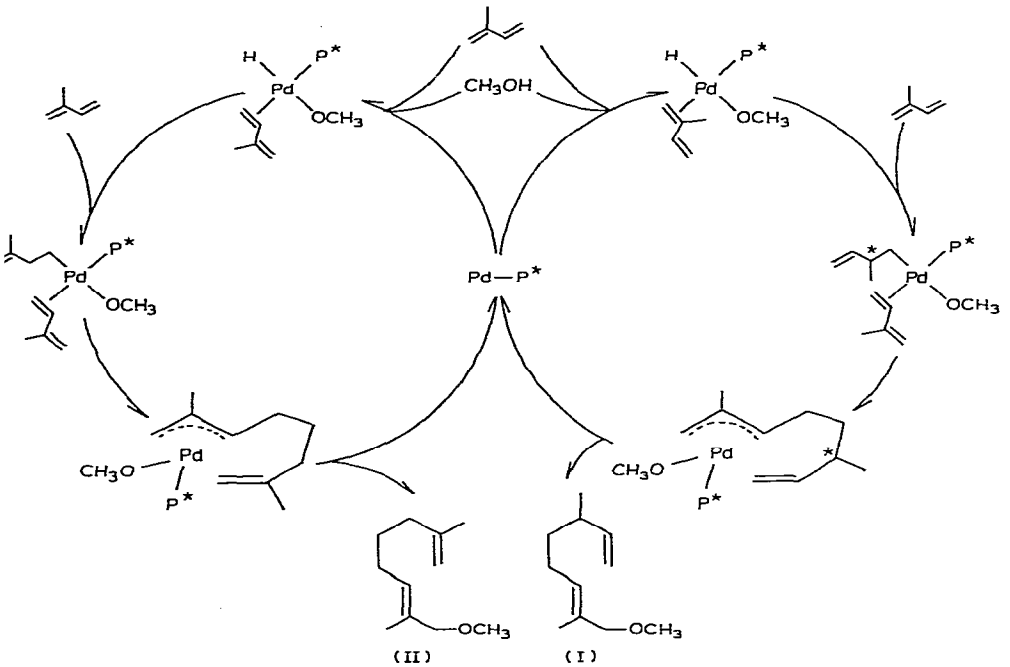
Other chiral phosphines were also tried, such as neomenthyldiphenylphosphine [12], menthyl diphenylphosphinite, and (*S*)-methylphenylbenzylphosphine [13]. Neomenthyldiphenylphosphine, an epimer of menthyldiphenylphosphine, gave the (—)-telomer I in 13% optical yield (Run 10). The other phosphines gave the (—)-telomer I in optical yields less than 5%. Unexpectedly, (*S*)-methylphenylbenzylphosphine did not increase the optical yield (only 1% optical yield).

This methoxy telomer I can be readily converted to (—)- or (+)-citronellol, as shown in Scheme 1. Thus treatment of the methoxy telomer I ($[\alpha]_D$ = —1.26°, neat), prepared by the catalyst containing neomenthyldiphenylphosphine, with dichlorobis(tri-n-butylphosphine)nickel and sodium methoxide in 2-propanol at 80°C gave optically active 2,6-dimethyl-1,3,7-octatriene ($[\alpha]_D$ = —0.44°, neat) in 70% yield. This triene was selectively hydrogenated at the 1,4-position by tricarbonyl(methyl benzoate)chromium at 150°C to produce 2,6-dimethyl-2,7-octadiene ($[\alpha]_D$ = —0.72°, neat). Then optically active citronellol was obtained from the diene via the hydroboration-oxidation reaction ($[\alpha]_D$ = +0.49°, neat). The optical purity of the starting telomer I was therefore determined to be 13%.

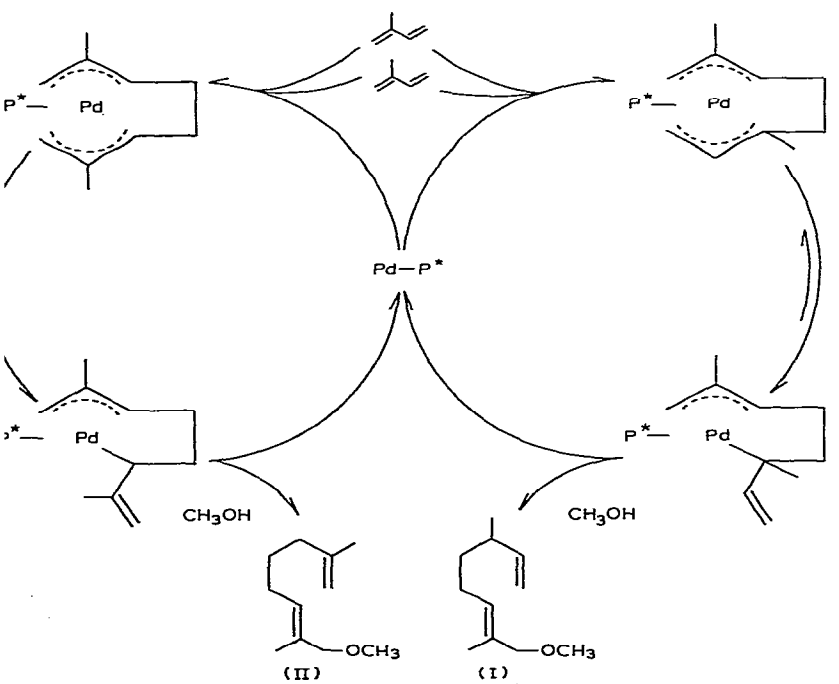
Various attempts to isolate some organometallic intermediates in this telomerization of isoprene were unsuccessful. But useful information was previously presented by Wilke et al. [14], who obtained a nickel complex with σ- and π-allyl groups from a nickel(0) complex and isoprene.



SCHEME 3



SCHEME 4



Two mechanisms appear reasonable for this telomerization reaction, both of which involve a palladium(0) species containing an optically active phosphine.

In one mechanism, methanol may oxidatively add to the zero-valent palladium to form a hydridomethoxopalladium(II) complex which reacts with isoprene to produce a methoxo(2-methyl-3-butenyl)palladium complex. In this step, the chirality might be introduced on to the tertiary carbon of the alkenyl group with the aid of the optically active phosphorus ligand. In the next step, isoprene is inserted into the metal—alkenyl bond to form a π-allylmethoxopalladium complex, which is followed by reductive elimination to produce the telomer I (Scheme 3).

The other mechanism we consider involves the coupling of two isoprene units on the palladium(0) species to form a palladium(II) complex with σ- and π-allyl groups where the chirality is introduced at the tertiary carbon of the σ-allyl group. The complex may undergo a nucleophilic attack by methanol to give the telomer I (Scheme 4).

In either mechanism, formation of the minor 'tail-to-tail' telomer II can be explained, as shown in Schemes 3 and 4, by another type of insertion of isoprene into the palladium—hydride bond or another type of coupling of two isoprene units. The details as to why the desired 'head-to-tail' methoxy telomer I is preferentially formed with palladium catalysts remain to be explained.

Experimental

All reactions were performed under a nitrogen atmosphere. Isoprene was dried and distilled over Drierite (anhydrous $CaSO_4$). Alcohols such as methanol, ethanol, and 2-propanol were distilled over the corresponding magnesium alkoxides which were prepared initially in situ from magnesium powder. Amines were dried over KOH pellets and distilled. Solvents such as ether, tetrahydrofuran (THF), and diglyme were purified by the usual methods, rigorously dried and distilled under a nitrogen atmosphere. (—)-*l*-Menthol, $NaOCH_3$, and boron trifluoride etherate were commercially obtained and used without further purification. (—)-Menthyl chloride [15], menthyldiphenylphosphine [11], neomenthyldiphenylphosphine [12], bis(π-allylpalladium chloride) [16], dichlorobis(tri-n-butylphosphine)nickel [17], and tricarbonyl(methyl benzoate)chromium [18] were prepared according to the reported methods.

A Hitachi 163 chromatograph was used for all GLC analyses to obtain quantitative yields of products and conversions of isoprene (N_2 carrier gas through 10% silicone DC-550 in a 3 m × 3 mm stainless steel column). Toluene was used as external standard in all GLC analysis. NMR spectra were recorded on a Hitachi R-40 Spectrometer (^1H, 90 MHz). Optical rotation was measured with a Perkin-Elmer Polarimeter 241.

Preparation of menthyldichlorophosphine ($MenPCl_2$)

A tetrahydrofuran (THF) solution of menthylmagnesium chloride, prepared from menthyl chloride (84 g, 0.48 mol) and activated magnesium turnings [19] (15 g) under reflux condition, was added to a THF solution (300 ml) of phosphorus trichloride (65.9 g, 0.58 mol) with cooling. The reaction mixture was stirred overnight and THF was removed by heating. The residue was extracted

vice with ether. The extract was concentrated under reduced pressure and stilled to give menthyldichlorophosphine (15 g, 13% yield, b.p. 83—84°C/0.1 mHg, $[\alpha]_D^{15} = -113.6°$, $c = 8.24$ in benzene).

eneral procedure for the preparation of menthyldialkylphosphines ($MenPR_2$)

In a typical run, an ether solution (50 ml) of the methyl Grignard reagent).12 mol) was added dropwise to an ether solution (70 ml) of menthyldichlo-phosphine (12 g, 0.05 mol) with cooling. The reaction mixture was allowed warm to room temperature, and was heated under reflux condition for 2 h. he reaction mixture was treated with aqueous ammonium chloride solution id extracted with ether. The extract was concentrated and distilled under duced pressure to give menthyldimethylphosphine [3] 2 g, 20% yield, b.p. 1°C/0.1 mmHg, $[\alpha]_D^{15} = -84.6°$, $c = 9.55$ in benzene).

Menthyldiethylphosphine (20% yield, b.p. 55—62°C/0.008 mmHg, $[\alpha]_D^{15} = 122.3°$, $c = 11.37$ in benzene), menthyldiisopropylphosphine [3] (20% yield, p. 93°C/0.1 mmHg, $[\alpha]_D^{15} = -87.8°$, $c = 5.68$ in benzene), and menthyl-phenylphosphine [11,12] (50% yield, m.p. 52.3—53.0°C, $[\alpha]_D^{15} = -88.5°$, = 1.77 in CH_2Cl_2) were prepared in the same manner. The data of NMR ectra and elemental analyses are summarized in Table 2.

BLE 2

MR DATA AND ELEMENTAL ANALYSES OF MENTHYLPHOSPHINES

osphine nPR$_2$	NMR (δ values in ppm from TMS) [a]	Elemental analyses. Found (Calcd.)		
		C	H	N
nPMe$_2$	0.8 (6H, d, CH_3—P)	71.94 (71.96)	12.65 (12.58)	
nPEt$_2$	0.9 (6H, t, CH_3—CH_2P), 2.8 (4H, qXd, CH_3—CH_2—P)	73.43 (73.64)	12.85 (12.80)	
nP(iso-Pr)$_2$	0.9 (12H, d, $(CH_3)_2$—CHP), 2.9 (2H, m, $(CH_3)_2$—CH—P)	74.21 (74.95)	13.06 (12.90)	
nPPh$_2$	7.3 (10H, m, C_6H_5—P)	81.37 (81.44)	8.95 (9.01)	
nP(OMe)$_2$	3.4 (6H, d, CH_3—OP)	61.44 (62.04)	11.00 (10.85)	
nP(OEt)$_2$	1.1 (6H, t, CH_3—CH_2OP), 3.7 (4H, qXd, CH_3—CH_2—OP)	64.90 (64.59)	11.23 (11.23)	
nP(O-iso-Pr)$_2$	1.17 + 1.29 (12H, d, $(CH_3)_2$—CHOP) 4.1 (2H, m, $(CH_3)_2$—CH—OP)	66.05 (66.63)	11.79 (11.53)	
nP(OPh)$_2$	7.0 (10H, m, C_6H_5—OP)	74.14 (74.13)	8.39 (8.20)	
nP(NMe$_2$)$_2$	2.6 (12H, d, $(CH_3)_2$—NP)	64.93 (65.08)	12.10 (12.09)	10.71 (10.84)

he resonance of the menthyl group was obtained in the following region; 0.8 (3H, d, CH_3—CH<, 0.9 I, d, $(CH_3)_2$—CH—), 1.5 (6H, m, —CH_2—), 2.0—2.2 (4H, m, —CH<).

General procedure for the preparation of dialkyl menthylphosphonites ($MenP(OR)_2$)

In a typical run, an ether solution (30 ml) of methanol (3.2 g, 0.1 mol) and pyridine (3.2 g, 0.04 mol) was placed in a 200 ml four-necked flask equipped with a reflux condenser, a dropping funnel, and a mechanical stirrer. An ether solution (20 ml) of menthyldichlorophosphine (9.6 g, 0.04 mol) was added dropwise to the solution with cooling. The reaction mixture was then allowed to warm to room temperature and stirred overnight. The ether solution was separated by filtration and the fractional distillation gave dimethyl menthylphosphonite (6.7 g, 72% yield, b.p. 49.5°C/0.005 mmHg, $[\alpha]_D^{15} = -64.8°$, $c = 7.02$ in benzene).

Diethyl menthylphosphonite (45% yield, b.p. 83—87°C/0.1 mmHg, $[\alpha]_D^{15} = -67.7°$, $c = 8.39$ in benzene), diisopropyl menthylphosphonite (61% yield, b.p. 68°C/0.017 mmHg, $[\alpha]_D^{15} = -60.1°$, $c = 9.73$ in benzene), and diphenyl menthylphosphonite (44% yield, b.p. 153°C/0.02 mmHg, $[\alpha]_D^{15} = -18.6°$, $c = 10.11$ in benzene) were prepared in the same manner. The data of NMR spectra and elemental analyses are summarized in Table 2.

Preparation of menthylbis(dimethylamino)phosphine ($MenP(NMe_2)_2$)

Excess dimethylamine (gas) was bubbled into an ether solution (350 ml) of menthyldichlorophosphine (5.7 g, 0.024 mol) with cooling and the reaction mixture was then stirred at room temperature overnight. After removing the white precipitate of $(CH_3)_2N^+H_2Cl^-$ by filtration, the filtrate was concentrated and distilled under reduced pressure to give menthylbis(dimethylamino)phosphine (3 g, 48% yield, b.p. 61.5°C/0.003 mmHg, $[\alpha]_D^{15} = -96.6°$, $c = 15.23$ in benzene). The data of NMR spectra and elemental analyses are summarized in Table 2.

Preparation of menthyl diphenylphosphinite ($MenOPPh_2$)

To a hexane solution (50 ml) of diphenylchlorophosphine (10 g, 0.05 mol) was added dropwise a hexane solution (50 ml) of *l*-menthol (18.7 g, 0.12 mol) and pyridine (9.5 g, 0.12 mol). Pyridinium salts were filtered off and then the filtrate was concentrated and distilled to give menthyl diphenylphosphinite (7 g, 40% yield, b.p. 210—215°C/0.0002 mmHg, $[\alpha]_D^{15} = -50.5°$, $c = 15.0$ in CH_2Cl_2).

General procedure for asymmetric telomerization

In a typical run, bis(π-allylpalladium chloride) (183 mg, 0.5 mmol), neomenthyldiphenylphosphine (324 mg, 1.0 mmol), isoprene (20 ml, 200 mmol), and methanol (20 ml) were placed in a 100 ml two-necked flask. After addition of sodium methoxide (1.0 mmol) the reaction mixture was stirred for 48 h at room temperature. Optically active 1-methoxy-2,6-dimethyl-2,7-octadiene (8.7 g, 46% yield) was obtained from the reaction mixture by fractional distillation (b.p. 61°C/5 mmHg, $[\alpha]_D^{15} = -1.26°$, neat).

Preparation of 2,6-dimethyl-1,3,7-octatriene

In a 100 ml four-necked flask equipped with a reflux condenser were placed dichlorobis(tri-n-butylphosphine)nickel (1.07 g, 2.0 mmol), sodium methoxide

3.5 g, 6.0 mmol), 2-propanol (20 ml), and the methoxy telomer I (10 g, 50 nmol, $[\alpha]_D^{15} = -1.26°$, neat). After the reaction mixture was stirred for 8 h at 30°C, it was poured into aqueous HCl solution. Distillation of the organic layer gave 2,6-dimethyl-1,3,7-octatriene (5.4 g, 70% yield, 52°C/7 mmHg, $[\alpha]_D^{15} = -0.44°$, neat).

Preparation of 2,6-dimethyl-2,7-octadiene

A hexane solution (50 ml) of 2,6-dimethyl-1,3,7-octatriene (5.4 g, 40 mmol, $[\alpha]_D^{15} = -0.44°$, neat) and tricarbonyl(methyl benzoate)chromium (0.54 g, 2.0 mmol) was heated at 150°C in a 100 ml stainless steel autoclave under H_2 pressure (50 kg/cm^2). After 30 h the reaction mixture was quenched by aqueous HCl solution. The organic layer was distilled to give 2,6-dimethyl-2,7-octadiene (5 g, 90% yield, b.p. 53°C/6 mmHg, $[\alpha]_D^{15} = -0.72°$, neat).

Preparation of citronellol

A diglyme solution (10 ml) of boron trifluoride etherate (3.03 g, 22 mmol) was added dropwise into a diglyme solution (50 ml) of 2,6-dimethyl-2,7-octadiene (6.9 g, 50 mmol, $[\alpha]_D^{15} = -0.72°$, neat) and sodium borohydride (0.6 g, 15 mmol) with cooling. The reaction mixture was stirred at room temperature for 2 h. Then, water (5 ml), an aqueous solution of sodium hydroxide (3 *N*, 20 ml), and an aqueous solution of hydrogen peroxide (30%, 20 ml) were successively added to the reaction mixture. The organic layer was separated and the aqueous layer was extracted with 50 ml of ether. Both etheral layers were combined and fractionally distilled to give optically active citronellol (4.7 g, 50% yield, b.p. 108°C/10 mmHg, $[\alpha]_D^{15} = +0.49°$, neat).

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