Synthesis of (+)- or (−)-Citronellol from Isoprene

By Masanobu Hidai,* Hisayasu Ishiwatari, Hiroshi Yagi, Eisuke Tanaka, Kazuhisa Onozawa, and Yasuzo Uchida*
(*Department of Industrial Chemistry, University of Tokyo, Tokyo, Japan*)

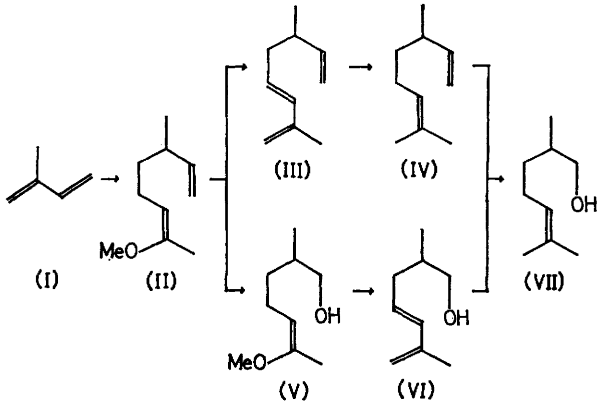
Summary (+)- or (−)-Citronellol was synthesized starting from isoprene in three or four steps.

Although the dimerization of isoprene (I) catalysed by transition-metal complexes has been studied extensively,[1–5] the structures of the dimers obtained were not in agreement with those of the natural terpenes. We have now synthesized citronellol (VII) by the two routes in the Scheme.

The dimerization of isoprene (I) with $\mathrm{PPh_3}$–Pd complexes to 1-alkoxy-2,6-dimethylocta-2,7-dienes such as (II) has been reported.[3] Treatment of (II) in $\mathrm{Pr^iOH}$ with $[\mathrm{NiCl_2(Bu^n{}_3P)_2}]$–NaOMe (1 : 3) as catalyst at 80 °C for 8 h gave compound (III) (*ca.* 80%). The palladium complex $[\mathrm{PdCl_2(Bu^n{}_3P)_2}]$ gave a lower yield of (III). Compound (VI) was similarly obtained from compound (V) (at 130 °C). Furukawa *et al.*[4] have recently reported that 1-isopropoxyocta-2,7-diene is converted into 2-methylenevinylcyclopentane with $[\mathrm{NiX_2(Bu^n{}_3P)_2}]$–$\mathrm{Bu^tOK}$ (X = Cl, Br, $\mathrm{NO_3}$).

Compound (III) could also be synthesized directly from (I) in one-step as follows. Compound (I) and $[\mathrm{PdCl_2}$-

(Bu$^n_3$P)$_2$]–NaOMe (1 : 3) in MeOH–Pr^{i}OH were stirred first at room temperature for 2 days and then at 80 °C for 8 h, to give (III) in 65% yield. If the mixture was heated immediately to 80 °C, a tail-to-tail dimer, 2,7-dimethylocta-1,3,7-triene was formed selectively. Miyake *et al.*[5] have recently found that (III) is the main product in the dimerization of (I) catalysed by [PdBr$_2$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$]–NaOPh–phenol at 150 °C. Hydrogenation of (III) and (VI) using carbonylchromium catalysts[6] such as [Cr(CO)$_3$(PhCO$_2$Me)] afforded compounds (IV) and (VII), respectively (*ca.* 90%). Hydration of (II) and (IV) by hydroboration gave (V) and (VII), respectively (*ca.* 60%).



Scheme

The dimerization of (I) catalysed by a combination of [Pd(π-C$_3$H$_5$)Cl]$_2$, NaOMe, and an optically active phosphine (1 : 2 : 2) yielded the dimer (II) in an optically active form in moderate yield. Neomenthyldiphenylphosphine ($[\alpha]_D$ +87·1°) gave the dimer (II) with $[\alpha]_D$ −0·84°, while menthyldiphenylphosphine ($[\alpha]_D$ −84·5°) gave (II) with $[\alpha]_D$ +1·71°. Optically active (VII) with $[\alpha]_D$ +0·49° (optical purity 8·6%) was derived from the former optically active dimer (Scheme). Analogously, (−)-(VII) (optical purity 17·6%) was derived from the latter optically active dimer.

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