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Preparation and oxidative polymerization of 2-methyl-6-geranylphenol

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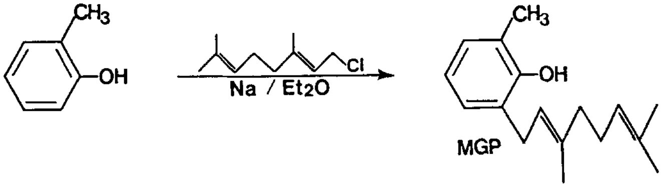
SUMMARY

2-Methyl-6-geranylphenol (MGP) was efficiently prepared by the reaction of o-cresol and 1-chloro-3,7-dimethyl-2,6-octadiene in the presence of alkali metal. MGP was oxidatively polymerized to poly(2-methyl-6-geranyl-1,4-phenyleneoxide).

INTRODUCTION

2,6-Disubstituted phenols provide corresponding poly(phenylene oxide)s (PPO) by means of oxidative polymerization in the presence of a copper-pyridine complex under oxygen atmosphere at room temperature$^{1-3)}$. Phenolic derivatives bearing isoprenoid substituents are often found in a wide range of natural materials, and are known to have physiological activities. These compounds are also interesting as a monomer of the oxidative polymerization and are expected to provide a new PPO derivative having bulky and rigid isoprenoid groups.



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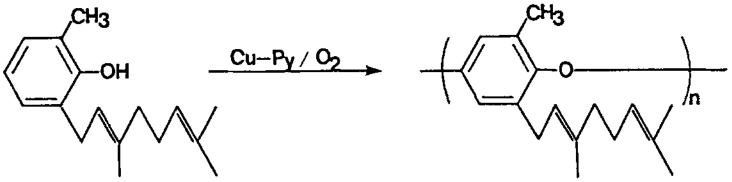

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We have already reported the preparation of phenols having allyl groups, such as 2,6-diprenylphenol and 2-methyl-6-butenylphenol, and their oxidative polymerization$^{4-6)}$. The present paper describes the preparation of 2-methyl-6-geranyl phenol (MGP) from o-cresol and 1-chloro-3,7-dimethyl-2,6-octadiene (geranyl chloride) in the presence of alkali metal in diethyl ether. The oxidative polymerization of MGP is also described.

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EXPERIMENTAL

Geranyl chloride was prepared as in lit[7]. 0.1 mol (15.4 g) of geraniol and 0.13 mol (34.1 g) of triphenylphosphine were dissolved in 90 ml of carbon tetrachloride. The solution was stirred and heated to reflux for 1.5 h. The reaction mixture was extracted with 100 ml of dry pentane. After evaporation of the solvent, the residue was distilled under reduced-prussure to give geranyl chloride(12.2 g, Yield 75 %). b.p. 45-48°C/ 0.4 mmHg. ^{1}H-NMR (CCl_4, TMS standard, δppm): 1.59, 1.66(6H, s, $C{=}C(CH_3)_2$), 1.72(3H, d, $C{=}C(CH_3)CH_2$), 2.03(4H, m, $-CH_2CH_2-$), 3.95(2H, d, CH_2Cl), 5.0(1H, m, $CH{=}C(CH_3)_2$) and 5.33(1H, t, $C{=}CHCH_2Cl$). Referential signals for geranyl chloride (CCl_4, TMS standard, δppm): 1.61, 1.67(6H, s, $C{=}C(CH_3)_2$), 1.71(3H, d, $C{=}C(CH_3)CH_2$), 2.05(4H, m, $-CH_2CH_2-$), 3.98(2H, d, CH_2Cl), 5.02(1H, m, $CH{=}C(CH_3)_2$) and 5.39(1H, t, $C{=}CHCH_2Cl$).

Typical procedure of MGP preparation was as follows. 0.01 mol (1.08 g) of distilled o-cresol was dissolved in 20 ml of dry diethyl ether. 0.01 mol (0.23 g) of metallic sodium was added and vigorously stirred for 0.5 h. 0.01 mol (1.73 g) of geranyl chloride was added slowly and the reaction mixture was refluxed for 1.5 h. Extraction of the reaction mixture with diethyl ether gave light yellow oil. The oil was distilled under reduced pressure giving 1.72 g of MGP (Yield 70.5%). b.p. 111-113°C/ 0.2 mmHg. M/e = 244. ^{1}H-NMR (CCl_4, TMS standard, δppm): 1.60, 1.66(s, 6H, $=C(CH_3)_2$), 1.73(s, 3H, $=(CH_3)-$), 2.06(m, 4H, $-CH_2CH_2-$), 2.17(s, 3H, $Ar-CH_3$), 3.27(d, j= 7Hz, 2H, $-CH_2-$), 5.22(t,j= 7Hz, 2H, $-CH{=}C$), 4.88(s, 1H, $-OH$), 6.36-6.93(m, 3H, Ar-H).

Geranylphenyl ether was separated by gas-chromatography. ^{1}H-NMR (CCl_4, TMS standard, δppm): 1.60, 1.66(s, 6H, $=C(CH_3)_2$), 1.72(s, 3H, $=(CH_3)-$), 2.05(m, 4H, $-CH_2CH_2-$), 2.19(s, 3H, $Ar-CH_3$), 4.42(d, j= 7Hz, 2H, $O-CH_2-$), 5.0(m, 1H, $-CH{=}C$), 5.42(t, 1H, $-CH{=}$), and 6.53-7.0(m, 4H, Ar-H).

Polymerization of MGP was carried out in benzene solution by the Cu(II)-pyridine catalyst, as follows. Cuprous chloride (50 mg) was dissolved in pyridine (8 ml) and 50 ml of benzene was added. This solution was stirred under oxygen to oxidize Cu(I) ion to Cu(II). 1.22 g of MGP was added to this catalyst solution under oxygen atmosphere and the mixture was stirred for ca. 0.5 h at 30°C. Then the reaction mixture was slowly poured with stirring to 500 ml of 10%-hydrochloric methanol, and the obtained brown viscous product was washed with methanol and dried in vacuo. ^{1}H-NMR of the polymer (CCl_4, TMS standard, δppm): 1.57, 1.69(9H, $-CH_3$), 1.94(3H, $-CH_3$), 2.0(4H, $-CH_2CH_2-$), 3.12(2H, $-CH_2-$), 5.08(2H, $-CH{=}$) and 6.34-6.63(2H, phenyl).

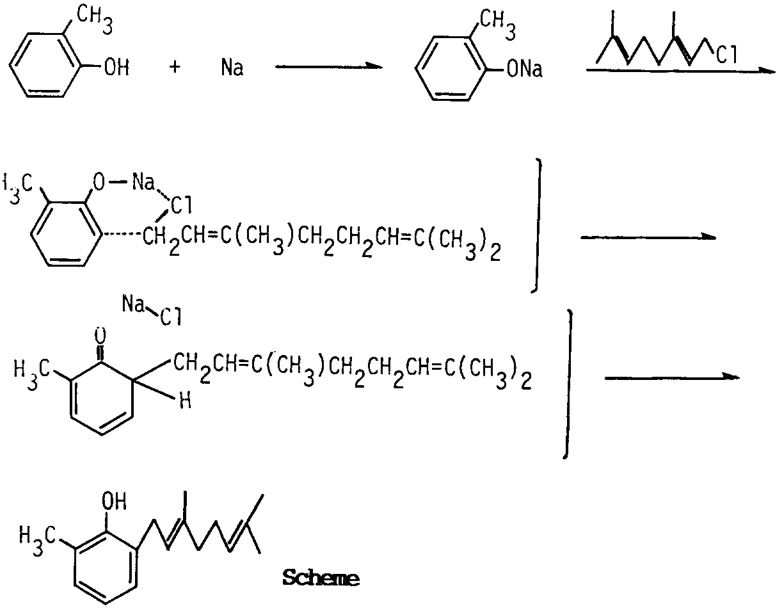
RESULTS and DISCUSSION

Time conversion curves of the products and starting o-cresol are plotted for the reaction in the presence of metallic sodium in Fig. 1. The yield of MGP increases with the reaction time and becomes constant after ca. 1.5 h. This reaction condition suppresses side-reactions to form by-products such as an ether- and chroman-type derivative. In the case of the reaction of geranyl chloride and phenol, ortho-geranyl phenol was obtained under the same conditions. However, 2,6-digeranyl phenol was not formed even by increasing the feed ratio of metallic sodium and geranyl chloride, probably because of steric hindrance of the geranyl group.

Effects of alkali-metal and solvent species were examined on the reaction of o-cresol and geranyl chloride to yield MGP (Table 1, 2). Metallic sodium provides MGP in a good yield. In diethyl ether as the reaction solvent, MGP is efficiently formed. The yield of the ether-type by-product, geranylphenyl ether, increases with the polarity of the solvent (Table 2). It can be assumed that O-alkylation is stimulated owing to a dissociation of the sodium phenoxide to phenolate anion and this occurs particularly in a high polar solvent such as methanol.

The reaction path of the MGP formation was considered, as has been described in the previous paper[5]. First, o-cresol and metallic sodium give sodium 2-methylphenolate. Then, the sodium 2-methylphenolate reacts equivalently with geranyl chloride to give MGP via the intermediate, 2-methyl-6-geranyl-3,5-cyclohexadienone.

Thus obtained MGP was oxidatively polymerized in the presence of the copper-pyridine catalyst under oxygen atmosphere to yield poly(2-methyl-6-geranyl phenylene oxide) in a similar manner as for 2,6-dimethylphenol.



Scheme

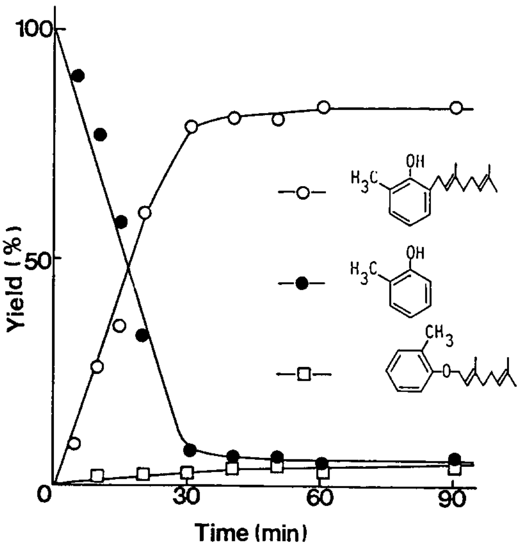


Fig. 1 Time-conversion curves of the MGP preparation
o-cresol; 0.01 mol, geranyl chloride; 0.01 mol, Na; 0.01 mol in 20 ml diethyl ether at 30°C

Table 1 Effect of metal species on the MGP yield

Metal	Yield(%)
Na	77.1
K	30.2
Li	trace

o-cresol; 0.01 mol, alkali metal; 0.01 mol in 15 ml ether at 35°C for 2 h (Na; 1.5 h).

Table 2 Effect of solvent species on the MGP yield

Solvent	Yield(%)
Ether	77.1
Bnezene	74.7
n-Hexane	58.4
THF	19.9
Methanol	4.4

o-cresol; 0.01 mol, alkali sodium; 0.01 mol in 15 ml solvent at 35°C for 1.5 h.

The polymeric structure, poly(2-methyl-6-geranyl-1,4-phenylene oxide), of the obtained brown viscous product was confirmed by ^{1}H-NMR spectrum (see Experimental section). It was also supported by the IR spectrum that absorption at 3400cm^{-1}, corresponding to the hydroxyl group, has almost disappeared, and new absorptions assigned to an ether bond (c-o-c) had been observed at 990 and 1180 cm^{-1}. Intrinsic viscosity in the benzene solution at 25°C was 0.14 (dl/g).

The geranyl groups in the polymer showed enough chemical reactivity, e.g. for an addition of bromine. Two bromine molecules were introduced per the monomer unit of the polymer, i.e. >98 % of the geranyl group was reacted with bromine. The brominated polymer is interesting for its self-extinguish property.

ACKNOWLEDGEMENT

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