A New Catalytic System for the Preparation of Chromanols

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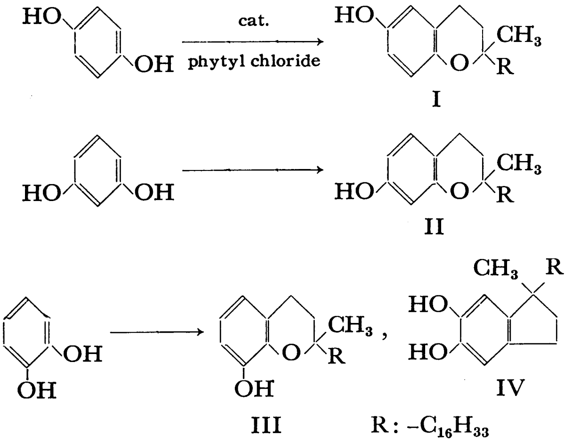
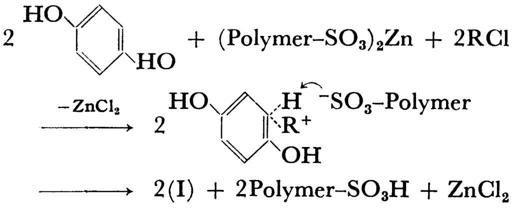
Synopsis. In the presence of the cation exchange resin complexes of metal ions, hydroquinone, resorcinol, and catechol reacted with phytyl chloride to give chromanols in good yields. The enhanced activity of the catalysts compared with the corresponding metal halides has been ascribed to the participation of the sulfonyl group in the abstraction of the proton on the benzene ring or the hydroxyl group. The catalysts were recycled several times with little loss of activity.

The study of anchoring homogeneous catalysts to a solid support has been developed on account of the ease in separation of product, the ability to carry out sequential catalytic reaction and positional selectivity.[1–3] It has been reported that the cation exchange resin complexes of metal ions are useful catalysts for the preparation of vitamin E.[4] In the course of studying the uses of the metal resin catalysts, it was found that these catalysts showed enhanced selectivity in the preparation of other chromanols compared with the corresponding metal halides.

In the presence of metal resin catalysts, the reaction of phytyl chloride with hydroquinone, resorcinol and catechol afforded I, II, and III, IV in good yields, respectively. Each product was characterized by elemental analysis, IR, NMR, and mass spectroscopy, the results of which are given in Table 1. The catalysts were recycled for use several times with little loss of activity, the results of which are summarized in Table 2, together with the results using metal halides for comparison. In the preparation of vitamin E from trimethylhydroquinone, little difference in selectivity was observed between the metal resin catalyst and metal halide.[4] The use of hydroquinone, resorcinol, and catechol in place of trimethylhydroquinone gave chromanols in poor yields when catalyzed by metal halides. The low selectivity has been attributed to the lower electron density of the benzene rings of hydroquinone, resorcinol, and catechol compared to trimethylhydroquinone. Therefore, the degradation of phytyl chloride by metal halides is more likely to occur than with trimethylhydroquinone. The yield of chromanol decreased in the order; resorcinol> hydroquinone> catechol which agrees with the order of electron density on the ortho or para position for the hydroxyl group.



The metal resin catalysts appear to enhance the activity of the substrate, resulting in higher yields of chromanols. The enhanced selectivity in the reaction catalyzed by the metal resin catalysts has been explained by assuming the participation of the sulfonyl group of the resin in the abstraction of the proton on the benzene ring (Scheme 1) or the hydroxyl group[5] (Scheme 2),



Scheme 1.

TABLE 1. SPECTRAL DATA AND ELEMENTAL ANALYSIS

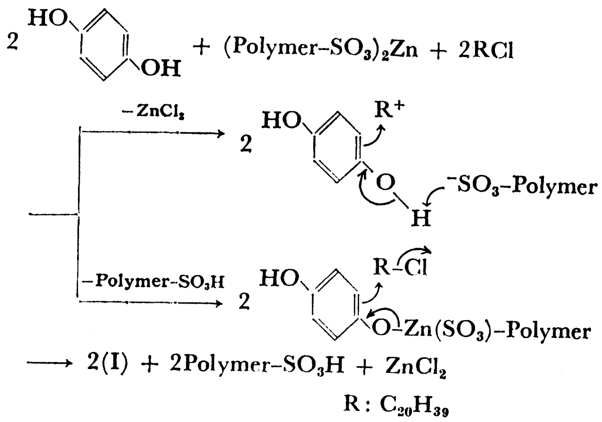
		I	II	III	IV
NMR (CCl_4) δ/ppm		0.85 (12H, d, isoprenoid CH_3), 1.00—1.60 (24H, bs, CH_3, isoprenoid CH_2, CH), 1.70 (2H, t, CH_2), 2.60 (2H, t, CH_2), 5.23 (1H, s, OH), 6.00—6.83 (3H, m, aromatic)	0.86 (12H, d, isoprenoid CH_3), 1.00—1.56 (24H, bs, CH_3, isoprenoid CH_2, CH), 1.70 (2H, t, CH_2), 2.63 (2H, t, CH_2), 5.00 (1H, s, OH), 6.26—6.69 (3H, m, aromatic)	0.85 (12H, d, isoprenoid CH_3), 1.00—1.66 (24H, d, CH_3, isoprenoid CH_2, CH), 1.80 (2H, t, CH_2), 2.73 (2H, t, CH_2), 5.53 (1H, s, OH), 6.50—6.83 (3H, m, aromatic)	0.87 (12H, d, isoprenoid CH_3), 1.00—1.60 (24H, d, CH_3, isoprenoid CH_2, CH), 1.77 (2H, t, CH_2), 2.66 (2H, t, CH_2), 5.50 (2H, bs, OH), 6.47 (1H, s, aromatic), 6.57 (1H, s, aromatic)
Mass (*m*/*e*)		388 (M^+), 163 (M^+—R,) 123	388 (M^+), 163 (M^+—R), 123	388 (M^+), 163 (M^+—R), 123	388 (M^+), 163 (M^+—R), 123
IR $\tilde{\nu}$/cm		3330, 2840, 1610, 1480, 1440, 1370, 1220, 1140	3400, 2920, 1630, 1600, 1520, 1470, 1390, 1150, 1000	3560, 2840, 1600, 1460, 1360, 1200,	3320, 2840, 1600, 1440, 1300, 1180
Found (Calcd) (%)	C	80.12 (80.35)	80.08 (80.35)	80.21 (80.35)	80.07 (80.35)
	H	11.36 (11.41)	11.21 (11.41)	11.33 (11.41)	11.16 (11.41)

Table 2. Effect of recycling catalyst

Substrate	Metal ion	Run	Yield/%[a)]
Hydroquinone	Zn	1	81
		2	77
		3	71
		4	70
	Sn	1	71
		2	74
		3	71
		4	70
	Al	1	63
		2	60
		3	58
		4	57
	$ZnCl_2$		38
	$SnCl_4$		52
	$AlCl_3$		18
Resorcinol	Zn	1	87
		2	84
		3	81
		4	77
	Al	1	73
		2	73
		3	70
		4	67
	$ZnCl_2$		25
	$AlCl_3$		38
Catechol	Zn	1	46 (49)[b)]
		2	44 (45)
		3	45 (38)
		4	43 (35)
	Sn	1	40 (52)
		2	40 (50)
		3	39 (45)
		4	36 (41)
	$ZnCl_2$		30 (32)
	$SnCl_4$		15 (0)

Substrate: 90 mmol, phytyl chloride: 90 mmol, catalyst: 45 mmol (as metal ion), benzene: 100 ml, temp: reflux temp, and time 3 h. a) By GLC. b) Yield of IV.

thereby facilitating substitution of the cation derived from phytyl chloride. In Scheme 2, the interaction of the $Zn(SO_3)$-polymer with the oxygen atom of the hydroxyl group may be included to activate the substrate. The latter mechanism (Scheme 2) appears however to be more plausible considering the ease of proton abstraction. The formation of IV is thought to be due to chelation between the two hydroxyl groups of catechol rather than a steric factor. The chelation presumably prevents the participation of the hydroxyl group in the formation of III.



Scheme 2.

Further studies on the detailed mechanism of this system are now in progress.

Experimental

GLC and atomic absorption spectra were recorded on a Hitachi 023 gas chromatograph equipped with a flame ionizer detector and a Hitachi 208 atomic absorption spectrometer, respectively. Amberlyst 15 (Rohm and Haas, 4.8 meq/g dry resin, in $-SO_3H$ form) was employed as cation exchange resin. The metal resin catalysts were prepared in the same way as described in a previous paper.[4)]

A typical procedure is described for the preparation of III and IV; A benzene solution (100 ml) containing catechol (9.9 g), phytyl chloride (28.5 g) and zinc resin catalyst (20 g, 2.25 mmol of zinc ion/g dry resin) was allowed to reflux for 3 h. After standing overnight, the catalyst was filtered off and washed with benzene and acetone. The filtrate was washed with 10% $NaHCO_3$ solution and water, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using benzene/hexane solution (1/2) as eluent, to give 12.1 g of III and 7.9 g of IV, respectively. The catalyst was again applied for the subsequent reaction.

In a similar way, other chromanols (I, II) were isolated.

References

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