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Optimization Conditions for the Synthesis of 1,1'Bis-(4-Hydroxy Phenyl) Cyclohexane

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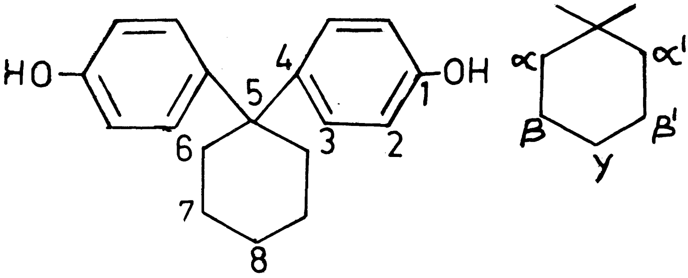
The optimization conditions for the reaction between cyclohexanone (0.05 mol) and phenol (0.1 mol) in the presence of varying proportions of the mixture of hydrochloric acid and acetic acid (2 : 1 v/v) were determined in the temperature range 40–70°C. The product was purifed from benzene and methanol (m.pt. 186°C). For better yield (> 85%), the optimum catalyst concentration is 10 ml. The condensation time is considerably shortened by increasing the catalyst concentration.

INTRODUCTION

Bisphenols are useful as intermediates for dyes, drugs[1,2], varnishes[3], constituents of veterinary medicines and fungistats[4], antioxidants, plasticizers and intermediates in many fields[5–7] and in control of coccidial infection[8]. Bisphenols are also industrially important in the production of thermally stable polymers and epoxy resins[9–11]. In our previous publication[12] we have reported the kinetics of formation of 1,1'-bis(3-methyl-4-hydroxy phenyl) cyclohexane by condensing cyclohexanone with *o*-cresol in the presence of varying mixtures of hydrochloric acid and acetic acid. In the present communication we have reported a simple synthesis of 1,1'-bis(4-hydroxy phenyl) cyclohexane **1** (bisphenol-C) by condensing cyclohexanone with phenol in the presence of varying mixture of HCl and AcOH at four different temperatures to establish optimum reaction conditions.



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EXPERIMENTAL

All the chemicals used were purified prior to use. The purity of bisphenol-C

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was checked by TLC using silicagel-G (Sisco-Chem.) and HPLC by LKB-Pharmacia (Sweden) HPLC-2150 pump column RP-8 Ultrapack Pharmacia 1.28 Ab-range and 278 λ_{max}. TLC (benzene-methanol 95 : 5 v/v) R_f 0.214 and HPLC (methanol) R_t 5.8 min. IR (KBr), ^1H NMR ^{13}C NMR spectra were scanned on a Shimadzu Dr-1, XL-100A spectrometer operating at 100.1 MHz and Varian CFT-20 using d_6-DMSO as solvent and TMS as internal reference, respectively. The mass spectrum was scanned on Varian Mat CH-7 Mass spectrometer.

The optimization conditions for the reaction between cyclohexanone and phenol was carried out in the presence of different proportions of mixture of hydrochloric acid and acetic acid as follows:

Cyclohexanone (0.05 mol), phenol (0.1 mol) and mixture of acids (2 : 1 v/v) were used at specified temperatures as shown in Table 1. The product formation time for each reaction mixture is noted in Table 1. The pink coloured product was recovered, washed with water to remove acids and then dissolved in 2M NaOH solution, kept overnight, filtered to remove resinous product, acidified,

TABLE 1
REACTION CONDITIONS, TIME AND % YIELD DATA FOR 1,1'-BIS-(4-HYDROXY PHENYL) CYCLOHEXANE.

Temperature (°C)	HCl/AcOH (2 : 1 v/v)	Time (min)	Yield (%)
40	2.5	305	21.6
	5.0	195	38.0
	7.5	140	56.0
	10.0	115	62.0
	12.5	95	76.1
	15.0	85	79.1
50	2.5	240	21.6
	5.0	140	43.3
	7.5	75	53.7
	10.0	65	60.5
	12.5	55	73.1
	15.0	45	81.3
60	2.5	190	14.9
	5.0	90	34.3
	7.5	75	41.0
	10.0	60	50.7
	12.5	45	61.2
	15.0	20	68.7
70	2.5	70	35.8
	5.0	40	62.7
	7.5	30	77.6
	10.0	25	86.6
	12.5	20	86.6
	15.0	15	89.5

filtered, washed with distilled water and dried at 90–100°C. The yield of each reaction is also reported in Table 1. The product was repeatedly recrystallized from benzene and finally the methanol solution was treated with charcoal to give fine shining crystals having m.pt. 186°C. (Found: C 80.41, H 6.91; calculated: C 80.59, H 7.46%). IR (ν cm^{-1}) 3580–3200, 3050–3000, 2920–2880, 1615, 1590, 1505, 1445, 1350, 1250, 1175, 1010, 910, 850, 730, 640, 585 and 560; ^{1}H NMR (DMSO-d_6): δ 8.5 (2H, s, 2X, OH), 6.9–6.6 (8H, m, Ar–H) 1.56 (4H, s, 4–α CH_2) and 2.28 (6H, s, β and γ CH_2), ^{13}C NMR: ppm, 152.88 (C_1), 113.21 (C_2), 125.84 (C_3), 137.57 (C_4), 42.48 (C_5), 35.09 (C_6), 24.30 (C_7), 20.39 (C_8) and m/e : 56, 57 (base peak), 69, 71, 81, 83, 85, 91, 97, 99, 111, 125, 251, 268 (M), 269 (M + 1).

RESULTS AND DISCUSSION

The variation of percentage yield against temperature and catalyst concentrations are shown in Figs. 1 and 2 respectively. From Fig. 1 it is evident that for

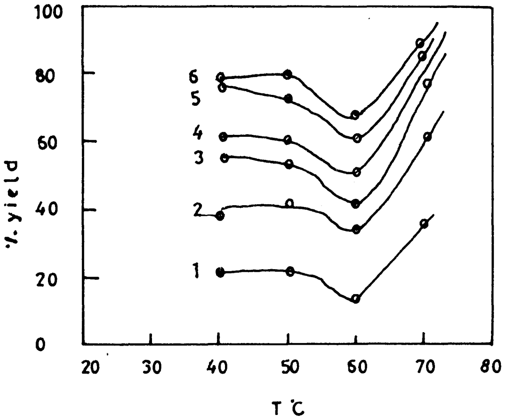

Fig. 1

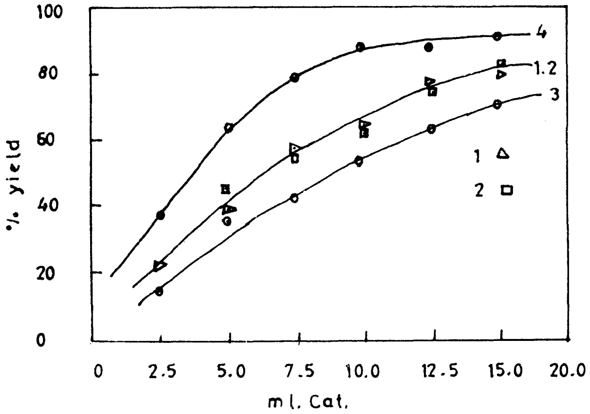

Fig. 2

the given catalyst concentration, percentage yield decreases, goes through a minimum and then increases with temperature. The minima appears at about 60°C. It is clear from the Fig. 2, that the yield increases with catalyst concentration and approaches asymptotic values after 10 ml of catalyst concentration at 70°C. The effect of catalyst concentration on the reaction time is shown in Fig. 3. The reaction time decreases exponentially with catalyst concentration at all

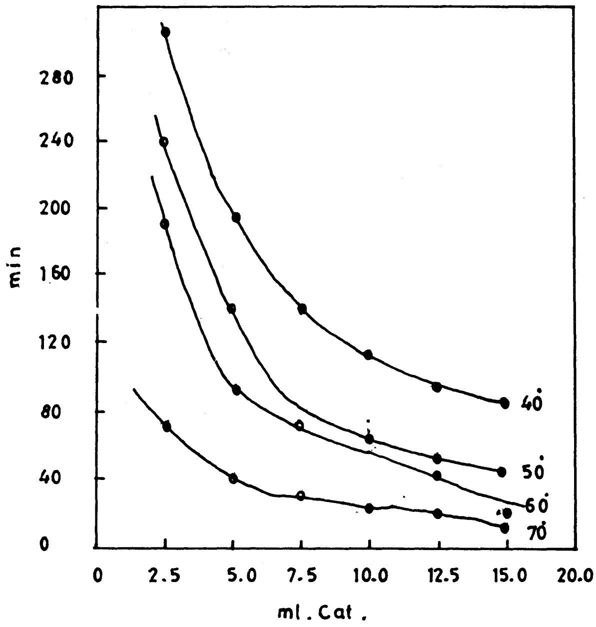

Fig. 3

temperatures studied. For better yield (> 85 %), we suggest an optimum catalyst concentration of 10 ml, while the optimum temperature is 70°C. At higher catalyst concentration reaction time is reduced from 30 to 15 min. There is another temperature region (40–50°C) over which the percentage yield is greater than 70% (Fig. 2) for catalyst concentration 12–15 ml but the reaction time is comparatively longer (45-95 min.) than the reaction time at 70°C for 10 ml catalyst concentration.

The methods reported in the literature[1,2,13–15] differ from our method in respect of reactants, catalyst concentrations, time and isolation of the product. In earlier works[14,15] the phenol concentration was in large excess and the reaction mixture was saturated with dry HCl for 3-4 hrs. below 40°C and reaction time was varied upto 4 weeks. The excess phenol was removed by vacuum distillation. In the present case the reaction was carried out in the presence of concentrated HCl and AcOH in the volume ratio 2 : 1 and the condensation time is much smaller (< 1 hr) than earlier work (1–4 weeks). The reaction of phenol with ketone in the presence of acid catalyst is a bimolecular reaction and takes place in two steps: (1) the addition of phenol to cyclohexanone giving $C_5H_{10}C(OH)-C_6H_5OH$ which is a slow reaction, and (2) the addition of a second molecule of phenol to this adduct with loss of H_2O to give $C_5H_{10}C\ [C_6H_5OH]_2$ which is a fast reaction.

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