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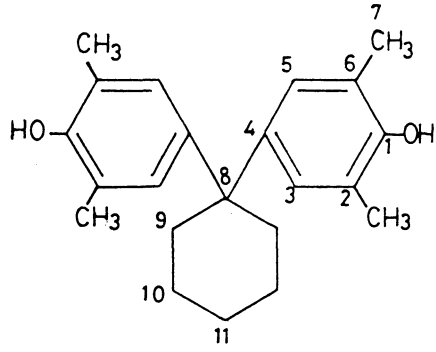
Optimization Reaction Conditions for Synthesis of 1,1′-Bis-(3,5-Dimethyl-4-Hydroxyphenyl) Cyclohexane

H.H. GARCHAR† and P.H. PARSANIA*
Department of Chemistry
Saurashtra University, Rajkot-360 005, India

The optimization conditions for the reaction between cyclohexanone (0.05 mol) and 2,6-dimethyl phenol (0.1 mol) in the presence of varying mixtures of hydrochloric acid and acetic acid (2 : 1 v/v) were investigated at four different temperatures, *viz.*, 40°, 50°, 60° and 70°C. The optimum reation conditions such as temperature, catalyst concentration and time have been investigated for obtaining yields greater than 80%. The purity and structure of the 1,1′-bis(3,5-dimethyl-4-hydroxyphenyl) cyclohexane is supported by TLC and HPLC and IR, ^{1}H NMR and ^{13}C NMR data.

INTRODUCTION

In continuation of our earlier work[1,2], we report in the present paper optimization conditions for synthesizing a simple 1,1′-bis(3,5-dimethyl-4-hydroxyphenyl) cyclohexane **1** by condensing cyclohexanone with 2,6-dimethyl phenol in the presence of Friedel-Crafts catalyst mixtures at the four different temperatures. The structure of the **1** is supported by IR, NMR and ^{13}C NMR spectral data.



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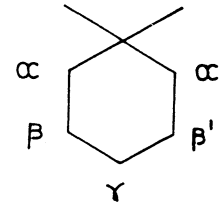

EXPERIMENTAL

All the chemicals used were of laboratory grade and were purified prior to use by the reported methods[3]. The purity of the **1** was checked by TLC (benzene-methanol, 85 : 15 v/v, R_f = 0.785) using silicagel-G (Sisco-Chem.) and HPLC

†M. and N. Virani Science College, Rajkot-360 005, India.

(methanol, R_t = 6.2 min.) [LKB-Pharmacia (Sweden), HPLC-2150 pump column: RP-8 Ultrapack Pharmacia 1.28 Ab. range. and 278 λ_{max}]. IR (KBr), ^1H NMR and ^{13}C NMR spectra were scanned on a Shimadzu DR-1, XL-100A (100.1 MHz) and Varian CFT-20 using deutero dimethyl sulphoxide as solvent and TMS as internal standard.

RESULTS AND DISCUSSION

The kinetics of reaction between cyclohexanone and 2,6-dimethyl phenol was carried out in the presence of different proportions of mixture of hydrochloric acid and acetic acid as follows: cyclohexanone (0.05 mol), 2,6-dimethyl phenol (0.1 mol) and mixture of acids (2 : 1 v/v) at a specified temperature as shown in Table 1. The product formation time for each reaction mixture is noted in Table 1.

TABLE 1
REACTION CONDITIONS, TIME AND % YIELD FOR 1,1'-BIS(3,5-DIMETHYL,4-HYDROXYPHENYL)CYCLOHEXANE.

Temperature (°C)	HCl/AcOH (2 : 1 v/v) (ml)	Time (min.)	Yield %
40	2.5	310	20
	5.0	250	38
	7.5	200	42.5
	10.0	170	56
	12.5	140	67
	15.0	120	69
50	2.5	270	22
	5.0	210	48.2
	7.5	165	64
	10.0	140	73
	12.5	115	75
	15.0	95	80
60	2.5	230	26
	5.0	170	58
	7.5	130	72.5
	10.0	105	78.5
	12.5	80	84
	15.0	60	88
70	2.5	190	24
	5.0	125	51
	7.5	95	68
	10.5	60	74.2
	12.5	40	80
	15.0	30	84

The product was recovered, washed with water to remove acids and then dissolved in 2M NaOH solution, kept overnight, filtered to remove resinous product, acidified, filtered and dried at 90°–100°C. The yield of each reaction is also reported in Table 1. The product was charcoalized in methanol and recrystallized

repeatedly from benzene, to give fine shining crystals having m.pt. 183°C, IR: 3510, 3490, 3050, 2920, 2850, 1600, 1480, 1435, 1376, 1322, 1300, 1288, 1268, 1236, 1188, 1176, 1140, 1116, 1020, 1000, 940, 890, 870, 856, 820, 780, 738, 684, 644, 596, 580 cm^{-1}; ^1H NMR (DMSO-D_6): δ 7.88 (s, –OH), 6.8 (s-Ar-H), 2.11 (s, $-CH_3$ and α, $-CH_2-$) and 1.41 (s, β and γ, $-CH_2-$); ^{13}C NMR: ppm, 150.50 (C_1), 123.47 (C_2–C_6), 126.45 (C_3–C_5), 139.40 (C_4), 17.02 (C_7), 43.78 (C_8), 36.74 (C_9), 26.06 (C_{10}), 22.76 (C_{11}).

The reaction conditions, time and % yield for 1,1'-bis(3,5-dimethyl,4-hydroxyphenyl)cyclohexane are reported in Table 1. It is evident from Table 1 that for 2.5 ml catalyst concentration % yield increases slightly with temperature and for the remaining concentrations of the catalyst % yield increases with temperature, reaches a maximum (*ca.* 60°C) and then decreases with temperature (Figures are not shown here); and it is also evident from Table-1 that the % yield increases with catalytst concentration and approaches a limiting value after 12.5 ml catalyst concentration over the temperature range studied. Reaction time decreases exponentially with catalyst concentration at all temperatures. For better yield (> 80%) we suggest the optimum conditions: 12.5 ml catalyst concentration, reaction time and temperature are 90 min. and 60°C, respectively. The mechanism[4] of condensation of ketones with phenols is well established and it is a SN^2 addition reaction.

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