

Kinetics of formation of 1, 1'-bis (3-methyl-4-hydroxy phenyl) cyclohexane

H H GARCHAR[†], H N SHUKLA^{††} and P H PARSANIA^{*}

Department of Chemistry, Saurashtra University, Rajkot 360 005, India

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

^{††}D. K. V. Arts and Science College, Jamnagar 361 008, India

MS received 7 April 1990; revised 11 October 1990

Abstract. The kinetics of reaction between cyclohexanone (0.05 mol) and *o*-cresol (0.1 mol) in the presence of varying mixtures of hydrochloric acid and acetic acid (2:1 V/V) were determined at four different temperatures: 40°, 50°, 60° and 70°C. The product was purified from benzene and methanol (m.p. 186°). The optimum reaction temperature, catalyst concentration and time have been determined for obtaining yields greater than 80%.

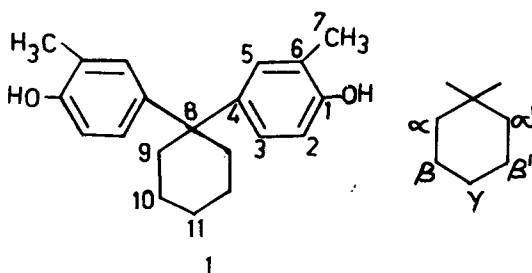
Keywords. Kinetics; cyclohexanone; *o*-cresol; catalyst.

1. Introduction

Condensation products of phenols and ketones are industrially important monomers in the manufacture of resins and plastics. Bisphenols have been synthesized by condensing phenols with aliphatic, aromatic and cyclic ketones in the presence of Friedel–Crafts catalyst. Alpine (1964) has condensed phenol, ketones, pulverized calcium chloride and boron trifluoride oxalic acid complex (376:58:40:4.26 parts) for 20 h at 50°C, the yield was in the range of 67–97%. Tumerman *et al* (1966) have condensed *o*-cresol and ketones in the presence of HCl and BF₃. The *o*-cresol to ketone molar ratio was in the range of 2:1 to 6:1 for 672 h at room temperature. They have reported that the % yield was ~15% more in case of reaction mixture saturated with HCl. Kozlov *et al* (1975, 1976, 1977) have used BF₃ as catalyst. They have reported a catalyst: *o*-cresol: cyclohexanone ratio of 6:3:0.53 and condensed it for 3 h at 40° to 45°C, the yield obtained being 90–94%. McGreal *et al* (1939), Farbenind (1927, 1929), Tumerman *et al* (1966), Farbenfabriken (1960) have used dry hydrochloric acid and acetic acid as catalyst. The ketone to phenol molar ratio was 0.5:1 in acetic acid and the mixture was saturated with dry hydrochloric acid for 3–4 h and kept in a closed vessel for varying periods upto 4 weeks at 50°C. The yields were reported in the range of 50–80%. Parsania *et al* (1985) have used HCl and AcOH (2:1 V/V) as catalyst. Bisphenols containing cardogroups (meaning loop) are very useful in synthesizing polymers with very specific properties such as enhanced thermal stability together with excellent solubility and film forming properties (Vinogradova *et al* 1971). The methods reported in the literature are disadvantageous in terms of reactants,

*For correspondence

catalyst concentrations, and time, and also inconvenient in isolation of the product. In the present paper we reported a simple synthesis by condensing cyclohexanone and *o*-cresol in the presence of various mixtures of HCl and AcOH at four different temperatures to establish optimum reaction conditions.



2. Experimental

All the chemicals used were of laboratory grade and were purified prior to use by the reported methods (Weisberger and Proskauer 1955). IR(KBr), ^1H NMR and ^{13}C NMR spectra were scanned on a Shimadzu DR-1, XL-100 A (100.1 MHz) and Varian CFT-20 using deuterio dimethyl sulphoxide as solvent and TMS as internal standard. Mass spectrum was scanned on a Varian Mat CH-7 mass spectrometer.

2.1 Kinetics of reaction

The kinetics of reaction between cyclohexanone and *o*-cresol was carried out in the presence of mixtures of hydrochloric acid and acetic acid as follows: cyclohexanone (0.05 mol), *o*-cresol (0.1 mol), and mixture of acids (2:1 V/V) at a specified temperature as shown in table 1. For each set the product formation time is also reported in table 1. The pink coloured product was isolated, washed with water to remove acids, dissolved in 2M NaOH solution, kept overnight and filtered to remove resinous material, acidified with dilute hydrochloric acid, filtered, washed with distilled water and finally dried at 90–100°C. The yield of each set is reported in table 1. The product was repeatedly recrystallized from benzene and finally the methanol solution was charcoaled to yield shining crystals having m.p. 186°. IR: 3520, 3400, 3060, 2900, 2850, 1600, 1500, 1470, 1450, 1405, 1335, 1295, 1270, 1220, 1195, 1120, 935, 902, 870, 735, 630, 610 cm^{-1} ; ^1H NMR (DMSO- D_6): δ 8.99 (2H, s, 2X-OH), 6.97–6.65 (6H, m, -ArH), 2.09 (10H, s, 2X- CH_3 and 2X α - CH_2 -) and 1.43 (6H, s, 2 β and γ - CH_2 -); ^{13}C NMR: ppm, 151 (C_1), 112.67 (C_2), 123.12 (C_3), 137.58 (C_4), 127.09 (C_5), 121.41 (C_6), 14.59 (C_7), 42.31 (C_8), 35.18 (C_9), 24.41 (C_{10}) 21.01 (C_{11}) and m/e : 56, 77, 82, 91, 105, 107, 110, 145, 165, 181, 253 (base peak), 254, 282, 296 (M), 298 ($M + 2$).

3. Discussion

Figures 1 and 2 show the variation of yield % against temperature and catalyst concentrations, respectively. For 2.5 ml catalyst concentration yield increases slightly

Table 1. Reaction conditions, time and % yield for 1,1'-bis(3-methyl-4-hydroxyphenyl) cyclohexane.

Temperature (°C)	HCl/AcOH (2:1 V/V) (ml)	Time (min)	Yield (%)
40	2.5	280	16.9
	5.0	195	36.5
	7.5	165	39.9
	10.0	140	50.0
	12.5	115	64.2
	15.0	90	66.2
50	2.5	160	17.6
	5.0	120	56.1
	7.5	95	71.6
	10.0	80	76.4
	12.5	70	81.0
	15.0	60	84.5
60	2.5	145	18.2
	5.0	100	45.3
	7.5	75	64.9
	10.0	60	70.9
	12.5	50	73.0
	15.0	40	77.7
70	2.5	100	20.3
	5.0	80	27.0
	7.5	65	40.5
	10.0	50	48.0
	12.5	35	54.0
	15.0	25	60.8

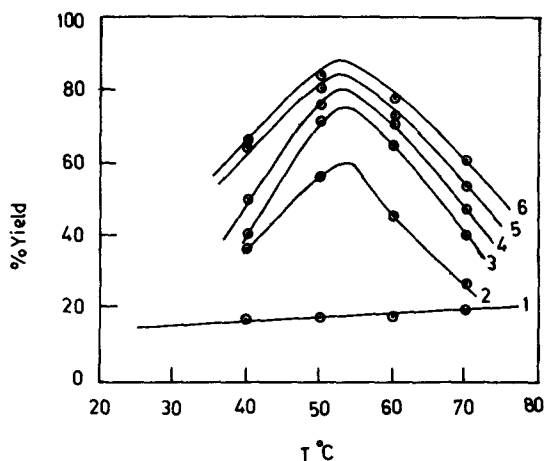


Figure 1. Variations of % yield against temperature, 1 - 2.5, 2 - 5.0, 3 - 7.5, 4 - 10.0, 5 - 12.5 and 6 - 15.0 ml catalyst concentration.

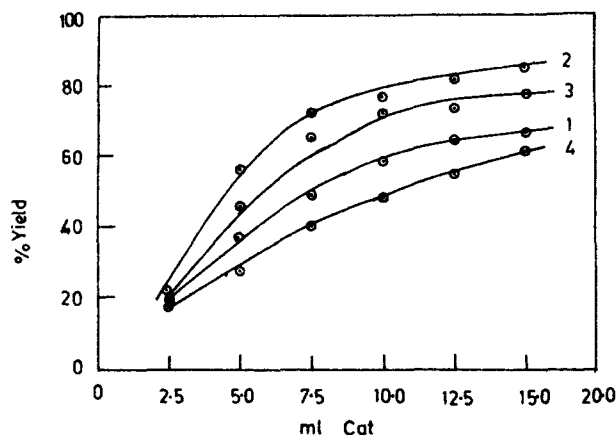


Figure 2. Variation of % yield against catalyst concentration 1 – 40°, 2 – 50°, 3 – 60° and 4 – 70°C.

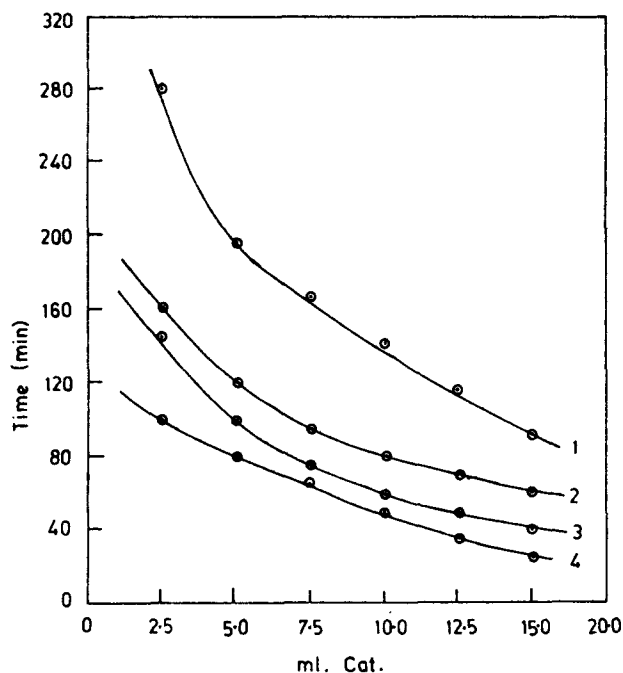


Figure 3. Effect of catalyst on reaction time, 1 – 40°, 2 – 50°, 3 – 60° and 4 – 70°C.

with temperature and for the remaining concentrations of the catalyst, yield increases with temperature, reaches a maximum ($\sim 53^\circ$) and then decreases with temperature. From figure 2 it is evident that the yield increases with catalyst concentration and approaches a limiting value after 10 ml concentration at all the temperatures studied. The effect of catalyst on the reaction time is shown in figure 3. Reaction time decreases exponentially with catalyst concentration at all temperatures and is the lowest at 70° .

For better yield (> 80%), we suggest an optimum catalyst concentration of 10 ml, while the optimum temperature is 53–55°. At higher catalyst concentration reaction time is reduced from 80 to 60 min.

Comparing the conditions of the work reported in the literature (Farbenind 1927, 1929; Mcgreal *et al* 1939), our method differs in the respect that in earlier work the reaction mixture in AcOH was saturated with dry HCl for 3–4 h and reaction time was upto 4 weeks; while in present case the reaction was conducted in the presence of concentrated HCl and AcOH in the volume ratio (2:1) and reaction time is shorter as compared to earlier work. The product formation in the presence of acid mixture is in two steps: (i) the addition of *o*-cresol to cyclohexanone giving $C_5H_{10}C(OH)[C_6H_3(CH_3)OH]$ which is a slow reaction, and (ii) the addition of a second molecule of *o*-cresol to this adduct with the loss of H_2O to give $C_5H_{10}C[C_6H_3(CH_3)OH]_2$ which is a fast reaction.

Acknowledgement

The authors are grateful to the Central Drug Research Institute, Lucknow, and the Regional Sophisticated Instrument Centres at Bombay and Madras for ^{13}C NMR, 1H NMR and mass spectra.

References

- Alpine Chemische A G 1963 *Br. Patent* 941995; 1964 *Chem. Abstr.* **60** 7957
Farbenind A G 1927 *Ger. Patent* 467728; 1929 *Chem. Abstr.* **23** 1729
Farbenind A G 1928 *Fr. Patent* 647454; 1929 *Chem. Abstr.* **23** 2540
Farbenfabriken 1958 Bayer Akt.-Ges. Ger-1, 031, 788. June 12, 1958 Addn. to Ger. 1,027,205; 1960 *Chem. Abstr.* **54** 19603d
Kozlov N S, Klein A G and Sukhodolova V P 1973 *Khim. Khim. Tekhnol.* **2** 63; 1975 *Chem. Abstr.* **82** 97778 P 170256
Kozlov N S, Klein A G and Sukhodolova V P 1976 *Chem. Abstr.* **85** 176992u
Kozlov N S, Klein A G and Sukhodolova V P 1977 *Dokl. Akad. Nauk. SSSR* **21** 146; 1977 *Chem. Abstr.* **87** 4961
Mcgreal N E, Niederl V and Niederl J B 1939 *J. Am. Chem. Soc.* **61** 345
Parsania P H, Shah P P, Patel K C and Patel R D 1985 *J. Macromol. Sci. [A]* *Chem.* **22** 1495
Tumerman B M, Gervits E S and Vesela I V 1966 *Chem. Abstr.* **64** 4977f
Vinogradova S V, Salazkin S N, Chelidze G Sh, Slonimskii G L, Askadsky A A, Bichko K A, Komarova L I, Zhuraleva I V and Korshak V V 1971 *Plast. Massy* **8** 10
Weisberger A and Proskauer E S 1955 in *Techniques of organic solvents* (New York: Inter Science)