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NOTES

Physico-Chemical Studies on Some Industrially Important Bisphenols

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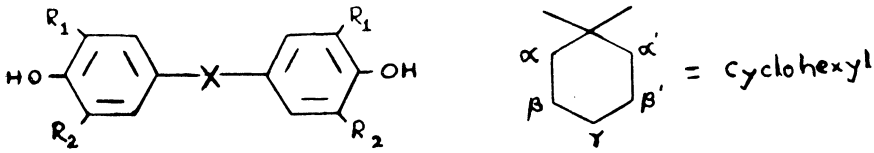
Bisphenols were synthesized by Fridel-Craft's condensation and bromination was carried out using ethanol as solvent at room temperature. Bisphenols were characterized by elemental, IR and NMR spectral data and a comparative thermal study was carried out by TGA.

Bisphenols are well known for their industrial applications in the preparation of thermally stable polymers and epoxy resins. The physical and chemical properties are strongly dependent on the structure of bisphenols.[1] It has been reported that resistance to high temperature is increased considerably by introducing cardo group in the bisphenol moiety[2]. Epoxy resins of bisphenols are useful in the preparation of paints and varnishes.[3] In present communication bisphenols of general scheme-I were synthesized by Fridel-Craft's condensation[4–6]. The structures of bisphenols were confirmed by elemental, IR and NMR spectral data, and kinetics of thermal degradation was carried out by thermogravimetric technique.



Scheme I

I. $X = -\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-$ $R_1 = R_2 = -H$

II. X = cyclohexyl, $R_1 = R_2 = -H$

III. X = cyclohexyl, $R_1 = -CH_3$, $R_2 = -H$

IV. $X = -\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-$ $R_1 = R_2 = -Br$

V. X = cyclohexyl, $R_1 = R_2 = -Br$

4,4'-Dihydroxydiphenyl sulphone[4](I), 1,1'-bis(4-hydroxy phenyl cyclohexane[5](II), and 1,1'-bis (4-hydroxy-3-methylphenyl) cyclohexane[6](III) were synthesized by Fridel-Craft's condensation technique. 4,4'-Dihydroxy

dibromophenyl sulphone(IV) and 1,1'-bis-(4-hydroxy-2,6-dibromophenyl) cyclohexane(V) were synthesized by reacting. I and II (20 g) with bromine (30 ml) in ethanol (100 ml) at room temperature for 2 hrs. I, IV and V were purified repeatedly from methanol-water, and II and III were purified from benzene and methanol. IR spectra were scanned in KBr on a Shimadzu DR-1 spectrometer, NMR spectra were scanned in DMSO-d_6 on a XL-100A spectrometer operating at 100·1 MHz using TMS as internal reference and elemental analyses were carried out at NCL Pune. Thermogravimetric investigations of I to V were carried out at heating rate of 10°C/min. in air.

IR spectral characteristic frequencies (ν_{max}, cm^{-1}) of I are 3367 cm^{-1} (—OH), 1360–1340 cm^{-1} (S=O, ν_{as} or OH), 1280–1220 cm^{-1} (C-O) 1140 cm^{-1} (S=O) ν_s), for II and III they are reported in our previous publication. The ν_{max} for C-Br are 520 cm^{-1} and 560 cm^{-1} for IV and V, respectively besides normal mode of vibrations.

NMR spectral data of I–V are reported in Table 1. In our previous publication[6], cyclohexyl and —CH_3 proton signals are misinterpreted. As cyclohexyl ring contains 10 protons out of which four (α-CH_2) protons

TABLE 1
NMR SPECTRAL DATA OF BISPHENOLS IN DMSO-d_6

Bisphenol	δ ppm	Types of protons	Multiplicity
I	10.57	—H	s
	6.94–7.02	—Ar	m
	7.75–7.83	—Ar	m
II	8.5	—OH	s
	6.9–6.6	—Ar	m
	2.28	—α —CH_2	s
	1.56	β and γ —CH_2	s
III	8.99	—OH	s
	6.65–6.97	—Ar	m
	2.09	—CH_3, α —CH_2	s
	1.43	β and γ —CH_2	s
IV	10.57	—OH	s
	7.83–7.75	—Ar	m
	7.02–6.94	—Ar	m
V	9.7	—OH	s
	7,46	—Ar	s
	2.15	α —CH_2	s
	1.41	β and γ —CH_2	s

are identical and remainder six (β and γ $-CH_2$) protons are identical. In III, $-CH_3$ and $-CH_2$ protons overlap and give signal at δ 2.09 ppm and β and γ $-CH_2$ proton signal at δ 1.43 ppm. Thus the bisphenol structures were confirmed by IR in conjunction with NMR spectral data.

The TG thermograms of I and IV showed two step decomposition, while II, III and V showed single step decomposition. The temperature range(s) for each is reported in Table-2. It is observed that thermal stability of bisphenols is approximately the same (260°C) and it is also found that there is no effect of X, R_1 and R_2 on the thermal stability. The method of Freeman-Anderson[7, 8] was followed in determining kinetic parameters such as energy of activation, E and order of the reaction, in Table 2.

TABLE 2
KINETIC PARAMETERS DERIVED FROM FREEMAN CARROLL METHOD AT HEATING RATE 10°C/min. IN AIR

Sample code	Temp. range(s) °C	Step-I n	Kinetic parameter step-II		
			E kcal/mole	n	E kcal/mole
I	(i) 264–420 (ii) 520–760	1.15	18.4	3.1	27.6
II	258–402	1.85	61.9	—	—
III	258–400	1.75	60.1	—	—
IV	(i) 260–398 (ii) 480–680	3.23	48.3	1.3	23.0
V	260–380	1.9	64.6	—	—

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REFERENCES

1. R. N. Johnson, A. G. Farnham, R. A. Glendinning, W. E. Hale and C. N. Marriam, *J. Polym. Sci.*, **A1, 5**, 2375 (1967).
2. V. V. Korshak, S. V. Vinogradova and Ya. Vygodskii, *J. Macromol. Sci. Rev. Macromol. Chem.*, **11**, 45 (1974).
3. E. A. Hassan, A. M. Naser and M. M. Wassel, *Paint India*, **28**, 13 (1978), *Chem. Abstr.*, **90**, 73352 (1979).
4. Tokai Electro Chemical Co. Ltd., JPn, Kokai Tokkyo Koho J, p. 82, **35**, 559, *Chem. Abstr.*, **97**, 91937 (1982).
5. P. H. Parsania, P. P. Shah, K. C. Patel and R. D. Patel, *J. Macromol. Sci. Chem.*, **A22**, 1495 (1985).
6. M. V. Rao, A. J. Rojivadia, P. H. Parsania and H. H. Parekh, *J. Indian Chem. Soc.*, **64**, 758 (1987).
7. E. S. Freeman and B. Carroll, *J. Phys. Chem.*, **62**, 394 (1958).
8. D. A. Anderson and E. S. Freeman, *J. Polym. Sci.*, **54**, 253 (1961).

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