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Aqueous High-Temperature Chemistry of Carbo- and Heterocycles. 10.[1] Aquathermolysis of Acyclic and Cyclic Phenol Ethers in the Presence of Sodium Bisulfite or Phosphoric Acid

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On aquathermolysis in a sulfite/bisulfite mixture, anisole and n-butyl phenyl ether show 27% and 19% cleavage conversion, respectively, with phenol as the only product. In 10% aqueous phosphoric acid, in addition to phenol, small amounts of alkylated products were also observed. When phenol was reacted with methanol or butanol in 10% phosphoric acid, the same slates of products were obtained as had been obtained from the corresponding ethers. As negligible conversions were seen in cyclohexane, acid-catalyzed ionic mechanisms are proposed. 2,3-Dihydrobenzofuran also gave phenol as the major product with some alkylphenols and dimers. Diphenyl ether showed no conversion under the conditions employed.

Introduction

Ether bonds are one of the major cross-links present in coals and kerogens.[2,3] The cleavage of ether cross-links in resources has immense potential for the synfuels industry.[4,5] In this paper, we report an aquathermolytic study of cyclic and acyclic phenol ethers. This work is an extension of our studies on the use of Bucherer reaction conditions for the dealkylation of phenols[1,6] in which we have investigated the action of aqueous bisulfite/sulfite mixtures on the reactivity of phenolic ethers. For comparison, we also carried out our reactions in cyclohexane (to detect thermal reactions), in water (to differentiate aqueous reactions), and in 10% aqueous phosphoric acid (to monitor acid catalysis).

The model compounds used in this study are anisole, diphenyl ether, n-butyl phenyl ether and 2,3-dihydrobenzofuran.

Experimental Section

The gas chromatographic behavior of all the compounds encountered in this work (starting materials and products) is summarized in Table I. Table II records the source and mass spectral fragmentation patterns of the authentic compounds used, either as starting materials or for the identification of products. Tables III and IV record the mass spectral fragmentation patterns of products for which authentic samples were not available and which were identified by comparison with literature MS data (Table III) or by deduction (Table IV). The aquathermolyses were conducted as previously described,[7] and the results are collected in Tables V–VII. Tables II and III have been deposited as supplementary material (see paragraph at end of paper regarding supplementary material).

Mass Spectral Assignments of Structures

Arrival at the final structures for the compounds in Table IV was reached by considering the fragmentation

(1) For part 9 of the series Aqueous High-Temperature Chemistry of Carbo- and Heterocycles, see: Katritzky, A. R.; Murugan, R.; Siskin, M. *Energy Fuels*, preceding paper in this issue.

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(6) Part 8 of the series Aqueous High-Temperature Chemistry of Carbo- and Heterocycles. Katritzky, A. R.; Murugan, R.; Siskin, M. *Energy Fuels*, in this issue.

(7) Part 1 of the series Aqueous High-Temperature Chemistry of Carbo- and Heterocycles. Katritzky, A. R.; Lapucha, A. R.; Murugan, R.; Luxem, F. J.; Siskin, M.; Brons, G. *Energy Fuels*, in this issue.

Table I. Structure and Identification of Starting Materials and Products

no.	t_R, min	structure[a]	mol wt	equiv wt	identification basis	response factor
1	0.60	toluene	92	92	Table II	1.12
2	1.21	anisole	108	108	Table II	0.79
3	1.76	phenol	94	94	Table II	0.76
4	1.95	2-methylanisole	122	122	Table III	0.71
5	2.05	4-methylanisole	122	122	Table III	0.71
6	2.47	*o*-cresol	108	108	Table II	0.79
7	2.54	2,3-dihydrobenzofuran	120	120	Table II	0.83
8	2.78	*p*-cresol	108	108	Table II	0.77
9	3.40	2-ethylphenol	122	122	Table II	0.78
10	3.74	4-ethylphenol	122	122	Table II	0.78
11	3.97	butyl phenyl ether	150	150	Table II	0.75
12	4.52	7-ethyl-2,3-dihydrobenzofuran	148	148	Table IV	0.75
13	4.94	5-ethyl-2,3-dihydrobenzofuran	148	148	Table IV	0.75
14	5.25	2-(1-methylpropyl)phenol	150	150	Table II	0.77
15	5.64	4-(1,1-dimethylethyl)phenol	150	150	Table II	0.77
16	5.72	4-(1-methylpropyl)phenol	150	150	Table II	0.77
17	6.55	diphenyl ether	170	170	Table II	0.71
18	7.34	2,5-bis(1-methylpropyl)phenol	206	206	Table III	0.72
19	7.86	2,4-bis(1-methylpropyl)phenol	206	206	Table III	0.72
20	8.07	2,5-bis(1,1-dimethylethyl)phenol	206	206	Table III	0.72
21	8.26	2,4-bis(1,1-dimethylethyl)phenol	206	206	Table IV	0.72
22	8.47	2,6-bis(1,1-dimethylethyl)phenol	206	206	Table III	0.72
23	8.68	2,6-bis(1-methylpropyl)phenol	206	206	Table III	0.72
24	8.79	2-(1,1-dimethylethyl)-4-(1-methylpropyl)phenol	206	206	Table III	0.72
25	9.02	2-(1-methylpropyl)-4-(1,1-dimethylethyl)phenol	206	206	Table IV	0.72
26	9.88	2,4,6-tris(1-methylpropyl)phenol	262	262	Table IV	0.73
27	10.34	2,4,6-tris(1,1-dimethylethyl)phenol	262	262	Table III	0.73
28	14.16	1-(2,3-dihydrobenzofuran-5-yl)-1-(2-hydroxyphenyl)ethane	240	120	Table IV	0.66
29	14.85	1-(2,3-dihydrobenzofuran-7-yl)-1-(2-hydroxyphenyl)ethane	240	120	Table IV	0.66

[a] See Schemes I–III for the structures of these compounds.

Table IV. Identification of Products from Mass Spectral Fragmentation Patterns

no.	compound	MW	fragmentation pattern, m/z (% relative intensity, structure of fragment ion)
12	7-Et-dihydrobenzofuran	148	148 (30, M); 133 (100, M − Me); 120 (40, M − C_2H_4); 105 (25, M − C_2H_3O); 91 (90, C_7H_7)
13	5-Et-dihydrobenzofuran	148	148 (50, M); 133 (100, M − Me); 119 (5, M − Et); 105 (20, M − C_2H_3O); 91 (10, C_7H_7)
21	2,5-bis(1,1-di-Me-Et)phenol	206	206 (10, M); 191 (100, M − Me); 176 (10, 191 − Me); 161 (5, 176 − Me); 146 (5, 161 − Me)
25	2-(1-Me-Pr)-4-1,1-(Me)$_2$-Et)phenol	206	206 (40, M); 191 (35, M − Me); 177 (100, M − Et); 162 (5, 191 − Et); 57 (20, C_4H_9)
26	2,4,6-tris(1-Me-Pr)phenol	262	262 (30, M); 247 (15, M − Me); 233 (100, M − Et); 205 (10, M − C_4H_9); 177 (10, M − C_6H_{13})
28	1-(2,6-dihydrobenzofuran-5-yl)-1-(2-hydroxyphenyl)ethane	240	240 (40, M); 133 (100, M − C_7H_7O); 120 (15, M − C_8H_8O); 107 (30, C_7H_7O); 91 (20, C_7H_7)
29	1-(2,3-dihydrobenzofuran-7-yl)-1-(2-hydroxyphenyl)ethane	240	240 (50, M); 133 (100, M − C_7H_7O); 120 (10, M − C_8H_8O); 107 (40, C_7H_7O); 91 (15, C_7H_7)

patterns, the starting materials, the reaction conditions, and reasonable mechanistic pathways from the starting material.

The products of Table IV can be classified into two sets: (i) substituted dihydrobenzofurans **12, 13, 28,** and **29** and (ii) substituted phenols **21, 25,** and **26.**

The dihydrobenzofurans **12** and **13** had the same M$^+$ at m/z 148. The addition of 28 units to the starting material, 2,3-dihydrobenzofuran (**7**), corresponds to the addition of an ethyl group. The base peak in both **12** and **13** was at m/z 133 arising from the loss of a CH_3 group. Both showed the characteristic (for dihydrobenzofuran)[8] m/z 91 peak. Hence, the structures 7-ethyl-1,2-dihydrobenzofuran (**12**) and 5-ethyl-1,2-dihydrobenzofuran (**13**) were assigned.

The dihydrobenzofurans **28** and **29** both showed M$^+$ at m/z 240 and similar fragmentation patterns. Products **28** and **29** are dimers of the starting material, dihydrobenzofuran (**7**). The presence of the dihydrobenzofuran (**7**) nucleus was confirmed by the observation of fragment peaks at m/z 120 for both; hence the structures 1-(2,3-dihydrobenzofuran-5-yl)-1-(2-hydroxyphenyl)ethane (**28**) and 1-(2,3-dihydrobenzofuran-7-yl)-1-(2-hydroxyphenyl)-ethane (**29**) were assigned (Scheme III).

The substituted phenols **21** and **25** both showed M$^+$ at m/z 206. The difference from the M$^+$ of the starting material, *n*-butyl phenyl ether (**11**), is equal to one butyl unit. The distinction between the *tert*-butyl and *sec*-butyl group substituent is that the *tert*-butyl-substituted compound shows loss of CH_3 groups, whereas the *sec*-butyl-substituted compounds shows loss of a CH_3 group as well as an C_2H_5 group.[9] Since the retention times and mass spectra of these compounds were different from those of their structural isomers reported in Table III, the structures 2,4-di-*tert*-butylphenol (**21**) and 2-*sec*-butyl-4-*tert*-butylphenol (**25**) were assigned.

The substituted phenol **26** had M$^+$ at m/z 262. The difference from M$^+$ of the starting material, *n*-butyl phenyl ether (**11**), is equal to two butyl groups. The base peak
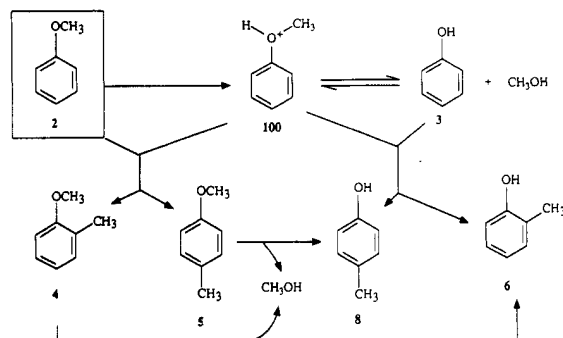
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Table V. Products of Anisole (2) and Phenol (1) Reactions at 250 °C for 3 days

no.	solvent additive (1 mol equiv) structure	anisole C_6H_{12}	anisole H_2O	anisole H_3PO_4 (10%)	anisole aq $NaHSO_3$ (satd) Na_2SO_3	phenol H_3PH_4 (10%) MeOH
1	toluene		0.1	0.7		
2	anisole	100.0	98.7	4.2	72.6	6.6
3	phenol		1.0	90.9	27.4	93.4
4	2-methylanisole		0.1	0.1		0.2
5	4-methylanisole		0.1	0.1		0.2
6	o-cresol			2.6		4.3
8	p-cresol			1.4		2.3
17	diphenyl ether					

Scheme I

Scheme II

Scheme III

was at m/z 233 arising from the loss of a C_2H_5 group. It also showed loss of CH_3, C_2H_5, and C_4H_9 units. Hence the structure 2,4,6-tri-*sec*-butylphenol (**26**) was assigned.

Results

Anisole (2) (Table V). All reactions were carried out at 250 °C over 3 days. In cyclohexane under these conditions anisole shows no reaction. However, in water, in aqueous sodium bisulfite/sulfite, and in phosphoric acid (10%), we find 1%, 27%, and 96% conversion, respectively. The major product in all three cases is phenol, although small amounts of alkylphenols (*o*- and *p*-cresols) and alkylanisoles (*o*- and *p*-methylanisoles) are also observed. The same distribution of alkylated products is obtained when anisole is replaced with a mixture of phenol and methanol and reacted in 10% phosphoric acid. Clearly an acid-catalyzed hydrolysis occurs: a 91% yield of phenol is obtained in the phosphoric acid reaction. Acid-catalyzed methylations then give rise to the small amounts of alkylated products.

Diphenyl ether (17) showed no reaction under all four [cyclohexane, water, aqueous Na_2SO_3/$NaHSO_3$, and H_3P-O_4 (10%)] sets of conditions.

**n-Butyl Phenyl Ether (11) (Table VI).** All reactions were done at 250 °C. Ether 11 shows no reaction in cyclohexane and almost no reaction in water (0.8%) over 3 days. In the sulfite mixture 19% conversion to phenol is obtained. In phosphoric acid (10%), 11 is completely converted in 3 days and gives 58% conversion after 1 day. With phosphoric acid, in addition to the expected product phenol, major amounts of alkylated phenols are also observed. The same mixture of alkylated products is obtained when the starting material n-butyl phenyl ether (11) is replaced with phenol and n-butanol and the reaction is conducted in 10% phosphoric acid.

2,3-Dihydrobenzofuran (7) (Table VII). All reactions were done at 250 °C for 3 days. In cyclohexane and in water we find 4% conversion. In the sulfite mixture and in 10% phosphoric acid we see 87% and 60% conversions, respectively. The major product in all cases is phenol. In
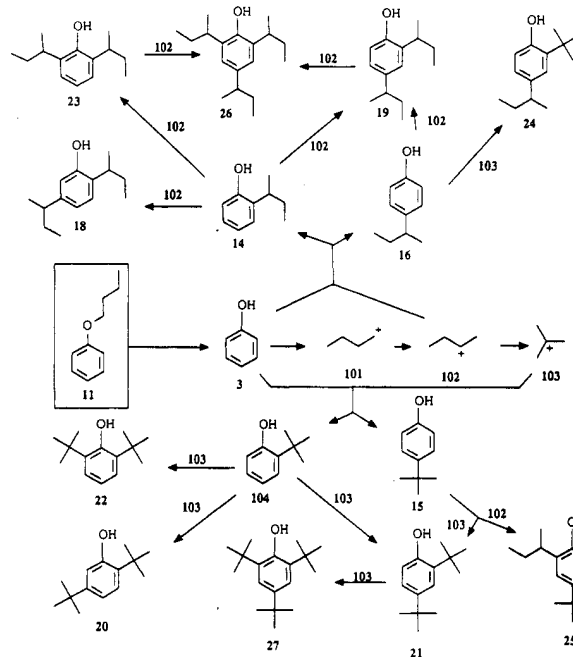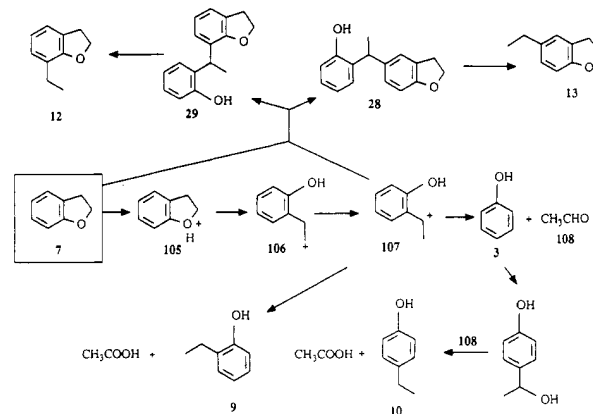
water and in aqueous sulfite mixture 2- and 4-ethylated phenols are also observed. In phosphoric acid, in addition to the ethylated phenols 9 and 10, ethylated dihydrobenzofurans 12 and 13 and two dimeric compounds 28 and 29 are observed.

Discussion of Results

The reactions are summarized in Schemes I–III. Structures not detected in the GC–MS system are given numbers ≥100. None of the compounds investigated showed appreciable reactivity on thermolysis in cyclohexane or on aquathermolysis in water alone. However,

Table VI. Products of Butyl Phenyl Ether (11) and Phenol (3) Reactions at 250 °C

no.	structure	n-butyl phenyl ether C_6H_{12} — 3	n-butyl phenyl ether H_2O — 3	n-butyl phenyl ether H_3PO_4 (10%) — 1	n-butyl phenyl ether H_3PO_4 (10%) — 3	n-butyl phenyl ether aq $NaHSO_3$ (satd) Na_2SO_3 — 3	phenol H_3PO_4 (10%) n-BuOH — 1
3	phenol		0.8	25.2	33.1	19.1	23.1
11	butyl phenyl ether	100.0	99.2	41.5	0.1	80.9	0.1
14	2-(1-Me-Pr)phenol			18.4	23.2		33.2
15	4-(1,1-(Me)$_2$Et)phenol			0.5	1.4		0.3
16	4-(1-Me-Pr)phenol			9.6	18.7		23.5
18	2,5-bis(1-Me-Pr)phenol				1.3		0.1
19	2,4-bis(1-Me-Pr)phenol			1.7	3.5		4.5
20	2,5-bis(1,1-(Me)$_2$Et)phenol				0.1		
21	2,4-bis(1,1-(Me)$_2$Et)phenol			1.1	2.7		1.1
22	2,6-bis(1,1-(Me)$_2$Et)phenol				0.1		
23	2,6-bis(1-Me-Pr)phenol				13.2		12.6
24	2-(1,1-(Me)$_2$Et)-4-(1-Me-Pr)phenol			0.5	0.7		
25	2-(1-Me-Pr)-4-(1,1-(Me)$_2$Et)phenol			1.4	1.4		0.9
26	2,4,6-tris(1-Me-Pr)phenol				0.2		0.1
27	2,4,6-tris(1,1-(Me)$_2$Et)phenol				0.2		0.4

Table VII. Products of 2,3-Dihydrobenzofuran Reactions at 250 °C for 3 days

no.	structure	C_6H_{12}	H_2O	H_3PO_4 (10%)	aq $NaHSO_3$ (satd) Na_2SO_3
3	phenol	4.2	3.8	47.8	76.5
7	2,3-dihydrobenzofuran	95.8	95.7	40.1	12.5
9	2-ethylphenol		0.5	0.5	8.9
10	4-ethylphenol			3.2	2.1
12	7-ethyl-2,3-dihydrobenzofuran			1.2	
13	5-ethyl-2,3-dihydrobenzofuran			4.5	
28	1-(2,3-dihydrobenzofuran-5-yl)-1-(2-hydroxyphenyl)ethane			1.1	
29	1-(2,3-dihydrobenzofuran-7-yl)-1-(2-hydroxyphenyl)ethane			1.5	

a dramatic increase in reactivity was found in the presence of aqueous sodium sulfite/bisulfite mixture and especially in phosphoric acid. In the aqueous sulfite/bisulfite system phenol is formed as the only product from anisole or butyl phenyl ether.

The products formed from anisole (2) in 10% phosphoric acid suggest an ionic mechanism. O-Protonation of the anisole gives a methyl cation donor species (100) which can react with water to give phenol (3) and methanol, but which also acts as a methylating agent to produce 4 and 5 from anisole and 6 and 8 from phenol. In turn 4 and 5 can also be hydrolyzed to 6 and 8 (Scheme I).

The products from the aquathermolysis of phenyl *n*-butyl ether (11) in phosphoric acid infer intermediacy of carbonium ions. The *n*-butyl cation (101) rearranges to the *sec*-butyl (102) and *t*-butyl analogues (103). The phenol from the hydrolysis is alkylated at the 2- and/or 4-positions by 102 or 103 to produce a wide range of derivatives as shown in Scheme II.

A similar initial sequence for 2,3-dihydrobenzofuran (7) gives successively carbonium ions 105, 106, and 107. Stabilized carbonium ion 107 reacts with 7 to give 28 and 29; alternatively 107 undergoes hydrolytic cleavage to CH_3CHO (108) and phenol (3). Acid-catalyzed dealkylation then converts 28 and 29 into 13 and 12, respectively, and provides an alternative entry to the ethylated phenols 9 and 10 as shown in Scheme III.

Conclusions

The cleavage reactions of anisole (2), *n*-butyl phenyl ether (11), and 1,2-dihydrobenzofuran (7) in aqueous bisulfite/sulfite mixtures gave phenol as the only product (or as the major product in the case of dihydrobenzofuran). No alkylated phenols are formed from anisole or from *n*-butyl phenyl ether (11) under sulfite mixture conditions, but these were seen when reactions were run in dilute phosphoric acid. The lack of reaction under thermal conditions (in cyclohexane) indicates that the aquathermolysis of these alkyl aryl ethers proceeds via ionic pathways. Most, if not all, the reactions studied were acid catalyzed.