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Aqueous High-Temperature Chemistry of Carbo- and Heterocycles. 2. Monosubstituted Benzenes: Benzyl Alcohol, Benzaldehyde, and Benzoic Acid

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Benzyl alcohol is not very reactive under aquathermolysis conditions, except in the presence of acids. Almost all the products are formed by ionic pathways. It undergoes reversible dehydration to dibenzyl ether, disproportionation to benzaldehyde and toluene, and self-benzylation to 2- and 4-benzylbenzyl alcohols. These benzylbenzyl alcohols can react further, but major amounts of polyalkylated products are formed by the mono- and dibenzylation of toluene to give a range of dibenzyltoluenes and (benzylbenzyl)toluenes. Small amounts of diphenylmethane and bibenzyl and their benzylated products are also formed. The behavior of benzyl alcohol in the presence of phenol, pyridine, benzaldehyde, and benzene is also studied and rationalized. Benzaldehyde is much less reactive, except in the presence of formaldehyde, and especially in the presence of formic acid, when considerable formation of benzyl alcohol occurs and siphoning into this reaction matrix is observed. Benzoic acid is still less reactive.

Introduction

We have focused on examining the aqueous chemistry of a series of families of organic carboxylic acids, aldehydes, and alcohols because of the prevalence of these redox systems in organic resource materials and their precursors, and because of the generality of their formation during the catagenesis of organic resources. Carboxylic acids and organic alcohols are abundant in type I and II kerogens as well as in lignites and subbituminous coals (type III kerogens). These functionalities are generally lost during maturation of kerogen to form petroleum and during thermal processing to form synthetic fuels. One goal of this research is to understand the chemical changes that take place and the influence of structure, and of autocatalysis by acids, bases, and redox reagents, especially those generated in situ, on the resource conversions.

This paper describes our findings on the chemistry of monosubstituted benzenes containing a single carbon atom (toluene, benzoic acid, benzyl alcohol, and benzaldehyde) in water and with various acidic and basic organic reagents using the methods and techniques described in part 1 of this series.[1] Three further papers in this series will report on the chemistry of monosubstituted benzenes in which a side chain of two linked carbon atoms is directly attached to the benzene ring and oxygenated at the β-carbon (part 5), the α-carbon (part 6), and at both the α- and β-carbons (part 7). In part 7 we will tie together the reactivity trends noted in these four papers (parts 2, 5-7).

The gas chromatographic data on the starting materials and the products of the thermolyses are recorded in Table I. The sources and purities of the starting materials are given in Table II.

The products listed in Table I were identified by one of the following methods.

(a) For the compounds of Table II, the method was by direct comparison of the GC retention time and of the MS fragmentation pattern with those of the corresponding authentic compound.

(b) The method used for the compounds of Table III (which were not compared with authentic specimens) was by comparison of the MS fragmentation pattern (peak mass and intensity) with literature MS data for the same compounds. (Tables II and III are deposited as supplementary material; see the paragraph at the end of the paper regarding supplementary material).

(c) For the compounds of Table IV, for which no suitable literature MS data were available, the method was by deduction from the MS fragmentation pattern. These deductions are discussed in the next section.

Mass Spectral Assignments of Structures

4-Benzylpyridine (13) shows the molecular ion peak at m/z 169 (50% relative intensity (r.i.)). It loses H· to give a base peak at m/z 168. The formation of tropylium cation at m/z 91 (60% r.i.) from the molecular ion due to the loss of a pyridyl radical supports structure 13.

Benzyl phenyl ketone (22) has a strong molecular ion peak at m/z 196. Loss of a neutral H_2O molecule gives a strong peak at m/z 178 that could be diphenylacetylene. Another cleavage pathway is the loss of CO from the M–1 ion giving a peak at m/z 167 (95% r.i.) that corresponds to the diphenylmethyl cation.

2-Benzylbenzaldehyde (23) shows the molecular ion peak at m/z 196 (60% r.i.). The loss of the CHO group from the molecular ion provides the base peak at m/z 167. The tropylium cation m/z 91 (55% r.i.) is also present.

4-Benzylbenzaldehyde (25) displays the molecular ion peak at m/z 196 (60% r.i.) and a fragmentation pattern similar to compound 23. The assignments are based on the fact that ortho isomers usually have lower boiling points (and retention times) than para isomers.

4-Benzylbenzyl acetate (31) shows the molecular ion peak at m/z 240 (80% r.i.), and loss of CH_2OCOCH_3 from this provides a base peak at m/z 165. It loses ketene from the molecular ion to give a peak at m/z 198 (45% r.i.) for the 4-benzylbenzyl alcohol cation. The formation of

(1) Katritzky, A. R.; Lapucha, A. R.; Murugan, R.; Luxem, F. J.; Siskin, M.; Brons, G. *Energy Fuels*, part 1; preceding paper in this issue.

Table I. Structure and Identification of Starting Materials and Products

no.	t_R, min	structure	mol wt	equiv wt	identification basis	response factor
1	0.45	PhH	78	78	Table II	1.09
2	0.53	PyH	79	79	Table II	0.80
3	0.60	$PhCH_3$	92	92	Table II	1.12
4	1.43	PhCHO	106	106	Table II	0.64
5	1.73	$PhCH_2OCH_3$	122	122	Table III	0.76
6	1.78	PhOH	94	94	Table II	0.76
7	2.14	$PhCH_2OH$	108	108	Table II	0.89
8	2.73	$HCOOCH_2Ph$	136	136	Table III	0.65
9	3.49	$PhCOOCH_3$	136	136	Table III	0.67
10	3.56	$PhCH_2OCOCH_3$	150	150	Table II	0.59
11	4.78	PhCOOH	122	122	Table II	0.51
12	6.93	$PhCH_2Ph$	168	84	Table III	0.85
13	7.94	4-benzylpyridine	169	169	Table IV	0.80
14	8.00	$PhCH_2CH_2Ph$	182	91	Table II	0.87
15	8.05	2-benzyltoluene	182	91	Table III	0.93
16	8.18	4-benzyltoluene	182	91	Table III	0.93
17	8.50	$PhCH_2OPh$	184	184	Table III	0.66
18	9.09	PhCOPh	182	91	Table II	0.66
19	9.52	$PhCH_2OCH_2Ph$	198	99	Table II	0.67
20	9.88	2-benzylphenol	184	92	Table III	0.75
21	10.06	$PhCH{=}CHPh$	180	90	Table II	0.83
22	10.16	$PhCH_2COPh$	196	98	Table IV	0.75
23	10.33	2-benzylbenzaldehyde	196	98	Table IV	0.59
24	10.46	$PhCO_2CH_2Ph$	212	111	Table III	0.62
25	10.58	4-benzylbenzaldehyde	196	98	Table IV	0.59
26	10.61	4-benzylphenol	184	184	Table III	0.75
27	10.75	$2\text{-}HOC_6H_4COPh$	198	198	Table III	0.58
28	10.82	anthracene	178	89	Table III	0.93
29	11.15	2-benzylbenzyl alcohol	198	99	Table III	0.75
30	11.75	4-benzylbenzyl alcohol	198	99	Table III	0.75
31	14.07	4-benzylbenzyl acetate	240	120	Table IV	0.61
32	14.58	4-benzyldiphenylmethane	258	86	Table IV	0.90
33	15.20	2,4-dibenzyltoluene	272	90.67	Table IV	0.89
34	15.30	2-benzyldibenzyl	272	90.67	Table IV	0.89
35	15.44	3-benzyldibenzyl	272	90.67	Table IV	0.89
36	15.59	2-[(2'-benzyl)benzyl]toluene	272	90.67	Table IV	0.89
37	15.96	3,4-dibenzyltoluene	272	90.67	Table IV	0.89
38	16.30	4-[(2'-benzyl)benzyl]toluene	272	90.67	Table IV	0.89
39	16.47	2,5-dibenzyltoluene	272	90.67	Table IV	0.89
40	16.73	2,6-dibenzyltoluene	272	90.67	Table IV	0.89
41	16.90	4-[(3'-benzyl)benzyl]toluene	272	90.67	Table IV	0.89
42	17.24	2-[(4'-benzyl)benzyl]toluene	272	90.67	Table IV	0.89
43	17.80	4-[(4'-benzyl)benzyl]toluene	272	90.67	Table IV	0.89
44	18.57	4-benzyldibenzyl	272	90.67	Table IV	0.89
45	21.82	4-benzylstilbene	270	90.00	Table IV	0.89
46	22.40	4-[4'-stilbenzyl]benzyl alcohol	286	95.3	Table IV	0.71
47	22.56	4-[(4'-benzyl)benzyl]benzyl alcohol	288	96	Table IV	0.71
48	22.74	4,4'-dibenzyldiphenylmethane	348	87	Table IV	0.86
49	23.30	4-benzyl-4'-(4-methylbenzyl)diphenylmethane	362	90.5	Table IV	0.86
50	23.91	4-[(4'-benzyl)benzyl]stilbene	360	90	Table IV	0.86

$PhCH_2C_6H_4CH_2^+$ from the molecular ion due to the loss of $OCOCH_3$ provides the peak at m/z 181 (35% r.i.), and this supports the assigned structure for **31**.

4-Benzyldiphenylmethane (**32**) displays the molecular ion peak at m/z 258 (60% r.i.). The formation of $C_6H_5CH_2C_6H_4^+$ from the molecular ion by loss of a benzyl radical provides the base peak at m/z 167.

Dibenzylated Toluenes. Compounds **33–44** are all of mass 272, corresponding to $C_{21}H_{20}$. The neutral compounds may be considered as $(3PhCH_2^+ - 2H^+ + H^-)$ and their structures, based on the mechanistic arguments discussed later, are given in Scheme I. Detailed consideration of the mass spectra of these isomers allowed their identification.

Compounds **36** and **42** are identified as ortho-benzylated toluenes in which the benzyl group has itself been benzylated. This assignment is based on the fact that o-benzyltoluene shows a characteristic peak at m/z 104 due to the formation of the $o\text{-}CH_2C_6H_4CH_2^+$ ion. In this set of compounds **33–44**, only compounds **36** and **42** provide a peak at m/z 104. Since the 2,2'-substituted isomer should have a lower boiling point (and retention time) than

the 2,4'-isomer, compound **36** is the 2,2'-isomer and compound **42** is the 2,4'-isomer.

The presence of a peak at m/z 105, which is due to the $p\text{-}CH_3C_6H_4CH_2^+$ ion, distinguishes compounds **38, 41,** and **43** from the rest of the isomers. The three possible isomers expected to give this fragment are 4-[(2'-, 3'-, and 4'-benzyl)benzyl]toluene. Using the same boiling point argument as above, compound **38** is the 4,2'-isomer, **41** is the 4,3'-isomer, and compound **43** is the 4,4'-isomer.

Compounds **34, 35,** and **44** are assigned on the basis that their molecular ions are relatively less intense than those from the other isomers (M^+ of 10%, 5% and 5% respectively). Additionally, they show a peak neither at m/z 104 nor at m/z 105. These compounds are therefore identified as o-, m-, and p-benzylbibenzyl, each of which should suffer easy scission at the weak bibenzyl bond and hence give unstable molecular ions. The individual assignments are based on the retention times.

Compounds **33, 37, 39,** and **40** are characterized as dibenzylated toluenes. Since the spectra of these compounds have strong molecular ions, they cannot be bibenzyls. The absence of peaks of mass 104 and 105 eliminates the

Table IV. Identification of Products from Mass Spectral Fragmentation Pattern

no.	compound	MW	fragmentation pattern m/z (% relative intensity, structure of fragment ion)
13	4-benzylpyridine	169	169 (50); 168 (100); 167 (45, M − H$_2$); 91 (55); 77 (25)
22	PhCH$_2$COPh	196	196 (100, M$^+$); 195 (60, M − H); 178 (74, M − H$_2$O); 167 (95); 165 (70); 152 (30)
23	2-benzylbenzaldehyde	196	196 (60, M$^+$); 167 (100, M − CHO); 165 (95); 152 (45); 115 (20); 91 (68)
25	4-benzylbenzaldehyde	196	196 (60, M$^+$); 167 (100, M − CHO); 165 (55); 152 (40); 115 (20); 91 (55)
31	4-benzylbenzyl acetate	240	240 (80, M$^+$); 198 (45, M − CH$_2$CO); 181 (35); 179 (70); 165 (100); 107 (80); 91 (65)
32	4-benzyldiphenylmethane	258	258 (60, M$^+$); 179 (10); 167 (100, M − PhCH$_2$); 165 (40); 152 (25); 91 (40)
33	2,4-dibenzyltoluene	272	272 (40, M$^+$); 181 (35, M − PhCH$_2$); 179 (100); 165 (48); 152 (10); 91 (22)
34	2-benzyldibenzyl	272	272 (10, M$^+$); 258 (70); 180 (32); 179 (35); 167 (100); 165 (40); 152 (20)
35	3-benzyldibenzyl	272	272 (5, M$^+$); 258 (38); 180 (13); 179 (15); 167 (100); 165 (35); 152 (18); 91 (20)
36	2-[(2'-benzyl)benzyl]toluene	272	272 (100, M$^+$); 257 (9, M − CH$_3$); 181 (60, M − PhCH$_2$); 167 (40); 165 (50); 152 (10); 104 (40)
37	3,4-dibenzyltoluene	272	272 (100, M$^+$); 257 (3, M − CH$_3$); 181 (90, M − PhCH$_2$); 167 (15); 165 (70); 91 (90)
38	4-[(2'-benzyl)benzyl]toluene	272	272 (100, M$^+$); 257 (10); 181 (95, M − PhCH$_2$); 167 (37); 165 (60); 152 (12); 105 (15); 91 (50)
39	2,5-dibenzyltoluene	272	272 (100, M$^+$); 257 (3, M − CH$_3$); 181 (97, M − PhCH$_2$); 166 (40); 165 (45); 91 (50)
40	2,6-dibenzyltoluene	272	272 (95, M$^+$); 181 (100, M − PhCH$_2$); 167 (25); 165 (30); 152 (5); 91 (10)
41	4-[(3'-benzyl)benzyl]toluene	272	272 (100, M$^+$); 257 (10, M − CH$_3$); 181 (85); 167 (50); 165 (40); 152 (5); 105 (15); 91 (10)
42	2-[(4'-benzyl)benzyl]toluene	272	272 (100, M$^+$); 257 (11); 181 (60, M − PhCH$_2$); 167 (50); 165 (40); 152 (10); 104 (40)
43	4-[(4'-benzyl)benzyl]toluene	272	272 (50, M$^+$); 181 (50, M − PhCH$_2$); 180 (60); 179 (70); 165 (70); 105 (13); 91 (100)
44	4-benzylbibenzyl	272	272 (5, M$^+$); 181 (60, M − PhCH$_2$); 180 (65); 165 (40); 91 (100)
45	4-benzylstilbene	270	270 (80, M$^+$); 192 (15, M − PhH); 179 (100, M − PhCH$_2$); 178 (65); 91 (20)
46	4-[(4'-stilbenzyl)benzyl alcohol	286	286 (10, M$^+$); 270 (50, M − O); 179 (95, M − PhCH$_2$O); 178 (50); 165 (40); 91 (100)
47	4-[(4'-benzyl)benzyl]benzyl alcohol	288	288 (15, M$^+$); 270 (25, M − H$_2$O); 192 (15); 179 (100); 165 (32); 91 (50)
48	4,4'-dibenzyldiphenylmethane	348	348 (15, M$^+$); 270 (20, M − PhH); 257 (10); 179 (100); 178 (25); 165 (15); 91 (80)
49	4-benzyl-4'-(4-methylbenzyl)-diphenylmethane	362	362 (35, M$^+$); 271 (10, M − PhCH$_2$); 270 (15); 179 (100); 178 (50); 165 (15); 91 (80)
50	4-[(4'-benzyl)benzyl]stilbene	360	360 (15, M$^+$); 269 (20, M − PhCH$_2$); 179 (65); 165 (20); 91 (100)

Scheme I
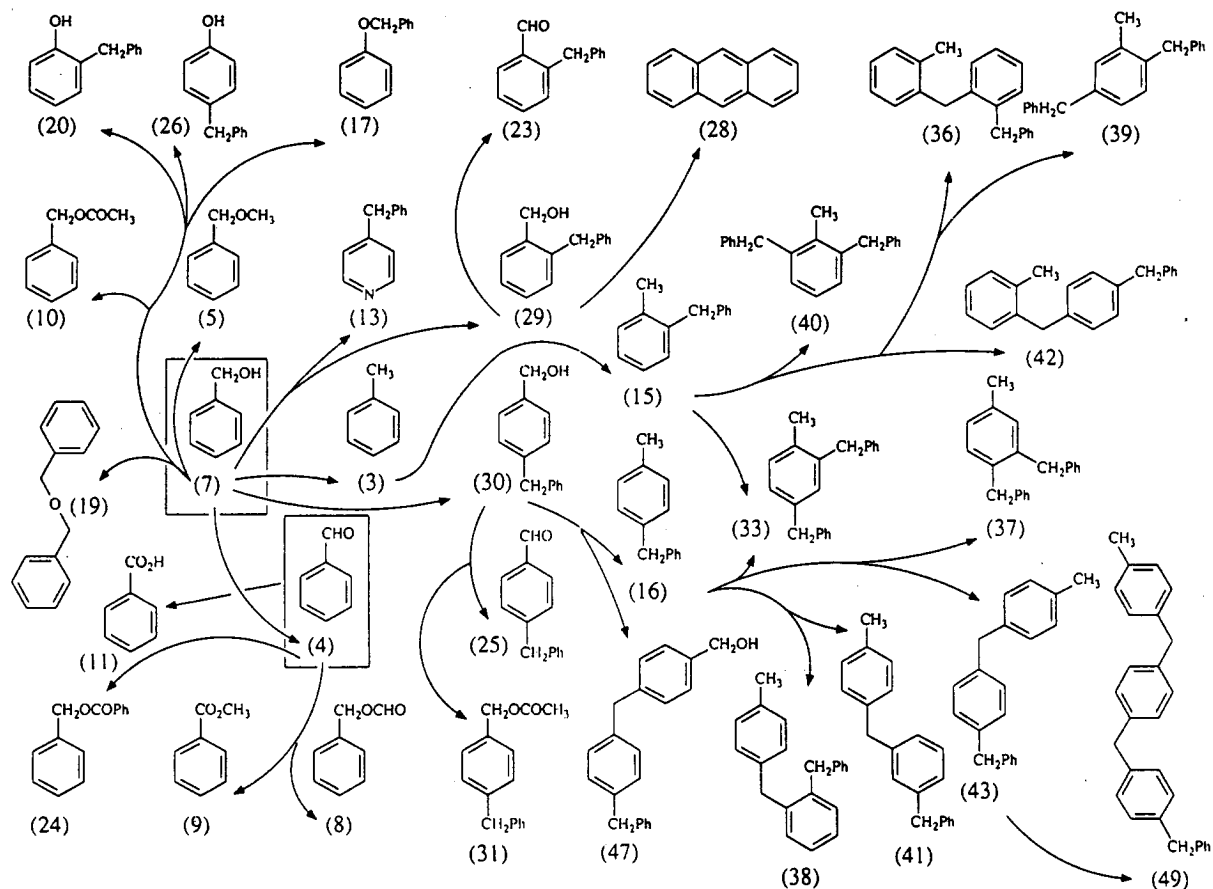
possibility of them being 2- or 4-benzyltoluenes. It is unlikely that 3-benzylated toluenes are formed since toluene is an ortho, para director. Therefore, the most probable structures for these compounds are various dibenzylated toluenes. The differences between the fragmentation patterns of these four isomers are insufficient to allow differentiation. Three of these compounds are almost certainly 2,4-, 3,4- and 2,5-dibenzyltoluene. The fourth one is probably the 2,6-isomer.

4-Benzylstilbene (45) is a dehydro analogue of compound 44. The molecular ion for 45 appears at m/z 270 (80% r.i.), and the fragmentation involves the loss of a benzyl radical leading to a base peak at 179 followed by an H⁺ to give a peak at m/z 178 (65% r.i.) which could be the molecular ion of diphenylacetylene.

4-[4'-Stilbenylbenzyl] alcohol (46) shows its molecular ion at m/z 286 (10% r.i.). It loses an oxygen atom to give a peak at m/z 270 (50% r.i.). The fragmentation pattern

is similar to compound **45**, and the base peak is the tropylium cation.

Compound **47** shows its molecular ion peak at m/z 288 (50% r.i.). Loss of a H_2O molecule from the molecular ion gives a peak at m/z 270 (25% r.i.). Further loss of a benzyl radical provides the base peak at m/z 179, so compound **47** could be a benzylated 4-benzylbenzyl alcohol.

4,4'-Dibenzyldiphenylmethane (**48**) shows the molecular ion peak at m/z 348 (15% r.i.). Loss of the benzyl radical followed by C_6H_6 provides a base peak at m/z 179.

Compound **49** displays its molecular ion peak at m/z 362 (35% r.i.). The base peak at m/z 179 is derived from the molecular ion by the loss of the benzyl radical and toluene. Since compound **49** has 14 mass units more than **48**, **49** could be 4-[(4'-benzyl)benzyl]toluene.

4-[(4'-Benzyl)benzyl]stilbene (**50**) shows the molecular ion at m/z 269 (20% r.i.) and 179 (65% r.i.) due to the loss of $PhCH_2$ and $CH_2C_6H_4CH_2Ph$ radicals from the molecular ion. The base peak is the tropylium ion.

Results

Benzene (1), Toluene (3), and Benzoic Acid (11). Benzene and toluene are unaffected by 5 days of heating at 250 °C in water. Toluene was also treated for 14 days at 350 °C in water alone, and in the presence of CF_3SO_3H (0.01 mol equiv) and of pyridine (1 mol equiv), but was completely unaffected. Benzoic acid (Table VII) is unchanged after 5 days at 250 °C, but it shows a minor amount of decarboxylation when heated at 350 °C for 6 h to give 0.1% benzene.

Benzoic Acid and Formaldehyde. In the presence of formaldehyde (1 mol equiv) at 250 °C, for 24 h, benzoic acid underwent 6.5% conversion mainly into methyl benzoate.

Benzyl Alcohol (7, Table V). On thermolysis in cyclohexane at 250 °C for 24 h, benzyl alcohol undergoes one major and several minor reactions:

(i) formation of 20.5% of dibenzyl ether by loss of water;

(ii) disproportionation into toluene (1.4%) and benzaldehyde (3.4%) with loss of H_2O; the presence of unequal amounts of these two compounds suggests that other products are undergoing reduction;

(iii) formation of a small amount of dibenzyl (0.2%);

(iv) formation of a small amount of 2-benzylbenzyl alcohol (**29**); this is probably the precursor of various compounds containing three phenyl rings—**38**, **40**, and **42**.

Thermolysis in cyclohexane for 5 days at 250 °C increased the conversion from 28% to 96.1%, suggesting some autocatalysis. All the foregoing products are found in much increased quantity; in particular the amounts of the condensation products with two and three phenyl rings increase markedly.

Aquathermolysis of benzyl alcohol shows a very similar slate of products to the thermolysis, but there are some significant quantitative differences. Whereas aquathermolysis is slightly faster than thermolysis after 1 day, it is considerably slower after 5 days, confirming the autocatalytic nature of the thermolysis. The amounts of disproportionation products (toluene and benzaldehyde) are much greater in the aquathermolysis, and the amount of dibenzyl ether is much smaller. In particular dibenzyl ether evidently undergoes fast aquathermolysis itself as the quantity after 5 days (1.7%) is much less than after 1 day (10.1%). Moreover, whereas the amount of compounds with two phenyl rings is larger in aquathermolysis than in thermolysis, for the disubstituted compounds the opposite applies.

The results strongly suggest that the so-called thermolysis is in reality mainly an aquathermolysis in which water produced in the reaction forms a separate phase with the benzyl alcohol in concentrated solution, and that this favors the formation of the higher molecular weight products. However, dibenzyl ether requires more water for its scission reaction; quite possibly, it comes into equilibrium with benzyl alcohol and water. Further products include a small amount of diphenylmethane (1.2%) and o- (1.0%) and p-benzyltoluene (0.6%). Aquathermolysis of benzyl alcohol at 250 °C, for 24 h, gave the disproportionation products toluene and benzaldehyde, benzyltoluenes, and some dibenzyl ether. When it is continued for 5 days at 250 °C, the disproportionation products predominate and dibenzyl ether levels are decreased by cleavage.

Benzyl Alcohol and Pyridine. The presence of pyridine (1 mol equiv) suppresses the aquathermolysis at 250 °C, and after 1 and 5 days, we find only 8.0% and 21.2% conversion, mainly by the disproportionation process. Only a small quantity of dibenzyl ether is formed.

Benzyl Alcohol and Phenol. In the presence of phenol (1 mol equivalent), at 250 °C, for 24 h, benzyl alcohol gave o- (1.8%) and p-benzylphenol (1.7%) as major products along with dibenzyl ether (2.3%) and benzyl phenyl ether (1.3%). When this reaction is continued for 5 days, the above products increase appreciably in amount and small quantities of dialkylated compounds are also formed.

Benzyl Alcohol and Acetic Acid. The presence of acetic acid (1 mol equiv) has a much more drastic effect on the aquathermolysis of benzyl alcohol. After 6 h at 250 °C, 59.4% is converted to a wide variety of products. There is considerable benzene (11.8%), benzaldehyde (2.8%), and also benzylbenzaldehydes **23** and **25**, a little toluene, and considerable dibenzyl ether (5.9%). The whole palate of dialkylated products is formed together with many monoalkylated ones. In 24 h, the reaction proceeds further, mainly in the same direction, except that the amount of dibenzyl ether decreases.

Benzyl Alcohol and Trifluoromethanesulfonic Acid. Benzyl alcohol in the presence of trifluoromethanesulfonic acid (0.001 mol equiv) at 250 °C, for 24 h, undergoes 89.8% conversion into a variety of mono- and dialkylated compounds in appreciable amounts. Particularly, compounds **38** and **48** are formed in major amounts in addition to dibenzyl ether (12.2%).

Benzyl Alcohol and Formic Acid. Formic acid (1 mol equiv) gives about the same degree of conversion as acetic acid. However, the product slate is considerably different: predominantly o- and p-benzyltoluene, very small amounts of aldehydes, and very considerable amounts of dialkylated products.

Benzyl Alcohol and Formaldehyde. Reaction of benzyl alcohol in the presence of formaldehyde (1 mol equiv) gives 35.2% conversion at 250 °C for 24 h. In addition to the expected products, this process yields 9.9% benzyl methyl ether, which can arise from the attack of a benzyloxy group on the protonated formaldehyde molecule.

Benzyl Alcohol and Acetic Acid in the Presence of Benzene or Benzaldehyde. Benzaldehyde (1 mol equiv) has a dramatic effect, suppressing the formation of all polyalkylated products: this is probably because it shifts the equilibrium $2PhCH_2OH = PhCHO + PhCH_3$ to the left and suppresses the formation of toluene, the benzylation of which is responsible for most of the higher molecular weight products. Benzyl alcohol and benzene (1 mol equiv) yield significant quantities (11.7%) of diphenylmethane (**12**).

Benzaldehyde (4, Table VI). Thermolysis in cyclohexane for 5 days at 250 °C gave benzoic acid (12.1%) as

Table V. Products of Aquathermolysis of Benzyl Alcohol

		C6H12	C6H12	H2O	H2O	H2O PyH	H2O PyH	H2O PhOH	H2O PhOH	H2O CH3CO2H	H2O CH3CO2H	H2O PhH	H2O CF3SO3H	H2O HCO2H	H2O HCHO
solvent additive (1 mol equiv) temp, °C		250	250	250	250	250	250	250	250	250	250	250	250	250	250
time, days		1	5	1	5	1	5	1	5	0.25	1	0.25	1	1	1
no.	structure														
1	PhH									11.8	20.5	9.0			
3	PhCH3	1.4	7.5	4.3	23.1	2.1	7.5	1.4	1.5	0.4	1.0	0.1	0.2	4.1	0.3
4	PhCHO	3.4	7.4	8.9	33.5	4.7	10.5	0.4		2.8	6.2	1.2	3.1	0.5	10.9
5	PhCH2OCH3														9.9
7	PhCH2OH	72.0	3.1	69.8	18.2	92.0	78.8	90.8	61.9	40.6	21.5	40.3	10.2	26.2	64.8
10	PhCH2OCOCH3									3.3	2.5	3.3			
12	.PhCH2Ph		1.2	0.1	0.5					1.1	1.8	11.7	1.7	2.4	0.4
13	4-benzylpyridine						0.1								
14	PhCH2CH2Ph	0.2								0.7	1.5				
15	2-benzyltoluene		1.0	0.8	6.4		0.5			1.7	1.3		0.4	18.4	
16	4-benzyltoluene		0.6	0.8	4.0		0.4			0.7	1.3		0.5	11.5	0.2
17	PhCH2OPh							0.7	1.7						
19	PhCH2OCH2Ph	20.5	67.1	10.1	1.7	1.0	2.1	2.3	8.4	5.9	2.5	15.8	12.2	3.8	6.6
20	2-benzylphenol							1.8	11.6						
21	PhCH=CHPh			0.3		0.1	0.4			0.4	1.8				0.7
22	PhCH2COPh			0.1	0.7							0.8			
23	2-benzylbenzaldehyde		0.4	0.2	0.9					0.6	0.4	3.2	2.7		1.5
25	4-benzylbenzaldehyde			0.3	0.3					0.3	0.7	2.3	4.4		
26	4-benzylphenol							1.7	10.3						
28	anthracene			0.1									0.5		2.2
29	2-benzylbenzyl alcohol	1.0	2.0	3.2	7.2					5.5	6.7	1.9	1.8		
30	4-benzylbenzyl alcohol		0.1		0.1					2.0	2.9	0.7	3.7		
31	4-benzylbenzyl acetate									0.7	0.8	0.4			
32	4-benzyldiphenylmethane									0.3	0.9		0.4	0.8	
33	2,4-dibenzyltoluene												1.7	3.3	
34	2-benzylbibenzyl									1.0	1.6			2.2	
35	3-benzylbibenzyl								0.1	0.1	0.4			1.6	
36	2-[(2'-benzyl)benzyl]toluene				0.2					0.3	0.6			3.0	
37	3,4-dibenzyltoluene									0.2	0.3			3.7	
38	4-[(2'-benzyl)benzyl]toluene	0.3	3.8	0.5	0.4				0.8	4.3	3.2	3.3	16.4	4.5	1.2
39	2,5-dibenzyltoluene								0.5	0.2	0.6				
40	2,6-dibenzyltoluene	0.7	1.8	0.2						1.7	1.4	1.2	6.1	4.2	0.5
41	4-[(3'-benzyl)benzyl]toluene							0.8	2.8	1.0	2.1		0.4		
42	2-[(4'-benzyl)benzyl]toluene	0.3	4.0	0.3				0.1	0.3	2.3	3.1	3.3	15.2	4.0	0.7
43	4-[(4'-benzyl)benzyl]toluene			0.1	1.1					2.7	3.1	1.5	0.7		
44	4-benzylbibenzyl			0.1	1.2					0.3	0.5				
45	4-benzylstilbene									1.1	1.6		2.8	2.3	
46	4-[(4'-stilbenyl)benzyl alcohol									1.9	2.2	0.7	3.2		
47	4-[(4'-benzyl)benzyl]benzyl alcohol									1.2	0.7		2.0		
48	4,4'-dibenzyldiphenylmethane									0.6	0.7		2.5	3.4	
49	4-benzyl-4'(4-methylbenzyl)diphenylmethane									1.2	1.3		4.5		
50	4-[(4'-benzyl)benzyl]stilbene									1.1	2.3		1.9		

a major product. Interestingly, a small amount of benzyl benzoate (24) (0.4%) is also formed by the Tischenko reaction. On heating in water at 250 °C for 5 days, benzaldehyde gives benzoic acid (14.0%) as a major product along with mono- and dialkylated compounds in smaller amounts.

Benzaldehyde and Pyridine. Aquathermolysis of benzaldehyde in the presence of pyridine (0.01 mol equiv) at 250 °C for 24 h gives only 4.9% conversion, leading to toluene, benzyl alcohol, and benzoic acid.

Benzaldehyde and Phenol. In the presence of phenol (0.01 mol equiv), aquathermolysis of benzaldehyde at 250 °C for 24 h gives only water-insoluble brownish yellow colored phenol–benzaldehyde polymer.

Benzaldehyde and Acetic Acid. Aquathermolysis of benzaldehyde for 24 h at 250 °C, in the presence of acetic acid (1 mol equiv), gives 36.4% conversion. Benzoic acid (33.8%) is the only major product formed in this reaction.

Benzaldehyde and Trifluoromethanesulfonic Acid. On heating at 250 °C, for 24 h, with trifluoromethanesulfonic acid (0.01 mol equiv), benzaldehyde gives 25.2% benzoic acid as a major product along with small amounts of benzene (0.3%), toluene (0.1%), and benzyl alcohol (0.4%).

Benzaldehyde and Formic Acid. Formic acid (1 mol equiv) at 250 °C for 24 h converts 74.3% of benzaldehyde mainly into benzyl alcohol (33.5%). In this reaction toluene (9.5%), o- (2.1%) and p-benzyltoluene (1.7%), and dibenzyl ether (5.1%) are also formed in addition to mono- and dialkylated compounds, which are undoubtedly produced by way of benzyl alcohol.

Benzaldehyde and Formaldehyde. Aquathermolysis of benzaldehyde in the presence of formaldehyde (1 mol equiv) at 250 °C for 24 h gives benzyl alcohol (5.9%) as the major product. Interestingly benzyl methyl ether (0.7%) is also formed in this reaction, together with small

Table VI. Products of Aquathermolysis of Benzaldehyde

no.	solvent additive (1 mol equiv) temp, °C time, days structure	C_6H_{12} 250 5	H_2O 250 5	H_2O PyH 250 1	H_2O PhOH 250 1	H_2O CH_3CO_2H $PhCH_2OH$ 250 0.25	H_2O CH_3CO_2H 250 1	H_2O CF_3SO_3H 250 1	H_2O HCO_2H 250 1	H_2O HCHO 250 1
1	PhH					6.4		0.3		
3	$PhCH_3$	0.4	1.1	0.1			2.6	0.1	9.7	0.3
4	PhCHO	86.5	81.2	95.1		0.6	63.6	72.7	25.7	92.3
5	$PhCH_2OCH_3$									0.7
7	$PhCH_2OH$		1.3	0.8		73.1		0.4	33.5	5.9
8	$HCOOCH_2Ph$								0.1	0.2
9	$PhCO_2CH_3$									0.2
10	$PhCH_2OCOCH_3$					7.3				0.3
11	$PhCO_2H$	12.1	14.0	3.6		5.7	33.8	25.2	9.2	0.1
12	$PhCH_2Ph$							0.1	0.2	
15	2-benzyltoluene								2.1	
16	4-benzyltoluene								1.7	
19	$PhCH_2OCH_2Ph$	0.2		0.4		5.3			5.1	
21	$PhCH{=}CHPh$		0.6						0.3	
22	$PhCH_2COPh$		0.6						0.2	
23	2-benzylbenzaldehyde	0.2						0.2	1.6	
24	$PhCO_2CH_2Ph$	0.4								
25	4-benzylbenzaldehyde	0.2						0.4	2.0	
29	2-benzylbenzyl alcohol		0.7						3.5	
30	4-benzylbenzyl alcohol		0.2						1.7	
32	4-benzyldiphenylmethane		0.1						0.2	
36	2-[(2'-benzyl)benzyl]toluene								0.2	
37	3,4-dibenzyltoluene								1.2	
38	4-[(2'-benzyl)benzyl]toluene		0.1						0.2	
39	2,5-dibenzyltoluene					1.2				
40	2,6-dibenzyltoluene					0.4				
41	4-[(3'-benzyl)benzyl]toluene		0.1							
42	2-[(4'-benzyl)benzyl]toluene								0.7	
43	4-[(4'-benzyl)benzyl]toluene							0.1	0.3	
44	4-benzyldibenzyl							0.4	0.5	
	polymer				100					

Table VII. Products of Aquathermolysis of Benzoic Acid

no.	solvent additive (1 mol equiv) temp, °C time, days structure	C_6H_{12} 250 5	H_2O 250 5	H_2O PyH 250 1	H_2O PhOH 250 1	H_2O CH_3CO_2H 250 1	H_2O CF_3SO_3H 250 1	H_2O HCO_2H 250 1	H_2O HCHO 250 1
9	$PhCO_2CH_3$								6.5
11	$PhCO_2H$	100	100	100	100	100	100	100	93.5

quantities of benzyl formate (8) and methyl benzoate (9) from the alternative crossed Tischenko reactions.

Discussion

Almost all the products are formed by ionic pathways. There are three major reaction types: (i) disproportionation of the CH_2OH group to CH_3 and CHO; (ii) dehydration of CH_2OH to give dibenzyl ether; (iii) benzylation of benzene rings.

All of these reactions release water, leading to a polar phase and autocatalysis in cyclohexane. Ether formation appears to be reversible so that dibenzyl ether acts as a reservoir of the alcohol. All the reactions, but especially iii, are acid catalyzed, and they are strongly inhibited by the presence of pyridine. The overall reaction pathways are combined in Schemes I and II.

At the left of Scheme I are shown products produced by interaction of benzyl alcohol with additives: o-, p-, and O-benzylated phenols (20, 26, 17) with phenol, benzyl acetate (10) with acetic acid, benzyl methyl ether (5) with formaldehyde, and 4-benzylpyridine (13) with pyridine. Dibenzyl ether (19) is formed reversibly. Benzylation of benzyl alcohols by benzyl cation forms the o- (29) and p-benzylbenzyl alcohols (30). These can each be oxidized to the corresponding aldehyde 23 and 25, respectively. The

acetate (31) of 30 was also detected in the benzyl alcohol and acetic acid system. Compound 29 is probably an intermediate in the formation of anthracene (28).

Reductions of the benzylbenzyl alcohols (29 and 30) in the appropriate system can give the benzyltoluenes 15 and 16 respectively; however, it is probable that 15 and 16 are mainly formed by benzylation of toluene itself, which is formed by disproportionation of benzyl alcohol (7) along with benzaldehyde (4). Further benzylations of 15 and 16 give the whole gamut of dibenzyltoluenes (40, 33, 37, and 39) and (benzylbenzyl)toluenes (42, 36, 38, 41, and 43).

Scheme II shows the probable reaction sequences of products (32 and 48) derived from further benzylation of diphenylmethane (12), itself formed by the benzylation of benzene. Other products are derived from stilbene (21) and from bibenzyl (14).

Benzyl alcohol is known[2,3] to convert toluene into 2,4-dibenzyltoluene (33, Scheme I) and other alkylation products. The process has been catalyzed by fluorosulfonic acid[2] and also by clay minerals.[3] The benzylation process

(2) Rueggeberg, W. H. C.; Catlin, W. E.; Cook, W. A. U.S. Patent 2,554,269, May 22, 1951; *Chem. Abstr.* 1952, 46, 140a.
(3) Petrova, L. N.; Shvarts, O. V. *Zh. Obshch. Khim.* 1950, 20, 2168; *Chem. Abstr.* 1951, 45, 7075c.

Scheme II
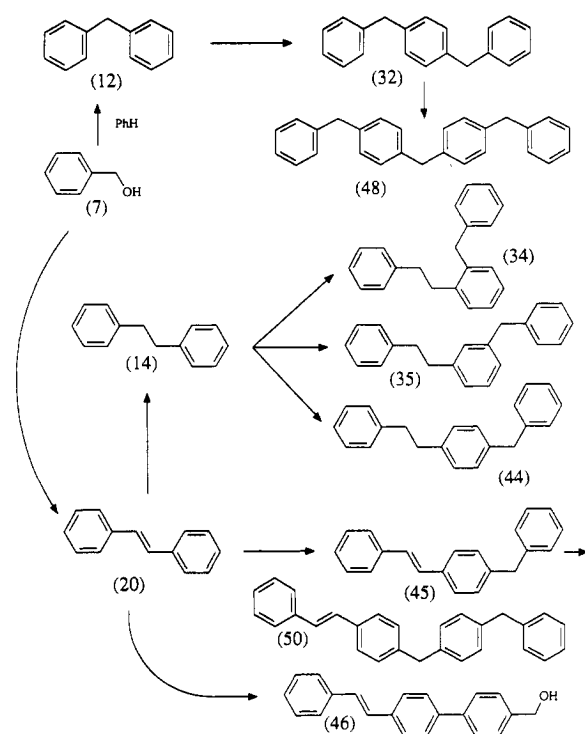
can also yield (benzylbenzyl)toluenes such as **43**.[4] The benzylation of bibenzyl (**14**, Scheme II) to give 4-benzyl-bibenzyl (**44**) has also been reported.[5]

On thermolysis in cyclohexane, benzaldehyde mainly undergoes disproportionation to give benzoic acid as the oxidation product and toluene as the product of reduction (the amount of toluene is probably lowered by handling losses). On aquathermolysis, benzaldehyde behaves very similarly, but a small amount of benzyl alcohol was also detected, together with a range of mono- and dialkylated products of benzyl alcohol, as expected in the more polar environment.

(4) Bredereck, H.; Lehmann, G.; Schonfeld, C.; Fritzsche, E. *Chem. Ber.* **1939**, *72B*, 1414.

(5) Cheltsova, M. A.; Petrov, A. D. *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* **1961**, 2209 [Engl. transl., 2065].

Acetic acid and trifluoromethanesulfonic acid accelerate the disproportionation of benzaldehyde.

In the presence of formic acid, benzaldehyde is reduced to benzyl alcohol, and this reacts further to yield the expected polyalkylated products, as discussed above. Formaldehyde also leads to reduction to benzyl alcohol, but now little acid-catalyzed conensation occurs.

Conclusions

Part 1 in this series described the autocatalytic reductions of pyridine-3-carboxaldehyde and 3-pyridylmethanol by hydride transfer from formic acid and formaldehyde, respectively, generated during aquathermolysis. The facile hydrolysis of benzyl acetate in water at high temperature is well-known. Benzyl alcohol alone reacts slowly in water, by an acid-catalyzed ionic pathway, but its reactivity is dramatically catalyzed in the presence of, e.g., acetic acid, which would be produced from the hydrolysis of benzyl acetate, to form large amounts of polyalkylated products. These reactions illustrate how autocatalysis can affect reaction pathways and can activate relatively unreactive molecules. We hypothesize that these types of auto-catalyzed chemistry represent possible parallel pathways by which petroleum can be produced in the pores of kerogens. The reactions of benzyl alcohol and benzaldehyde with various acidic and basic organic reagents described in this paper reinforce these conclusions.