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PHENOXENIUM IONS

IDENTICAL INTERMEDIATES IN THE ACID-CATALYZED SOLVOLYSIS OF N-TOSYL-O-ARYLHYDROXYLAMINES AND IN THE THERMOLYSIS OF N-ARYLOXYPYRIDINIUM SALTS

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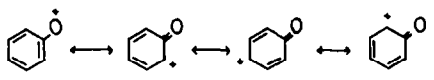
Abstract—The acid-catalyzed solvolysis of N-tosyl-O-arylhydroxylamines in aromatic solvents and the thermolysis of N-aryloxypyridinium salts involve common intermediates, phenoxenium ions, for the formation of hydroxybiphenyl derivatives. Diphenylethers are formed when the heterolysis of the N—O bonds is slow and the aromatic solvent has high nucleophilicity.

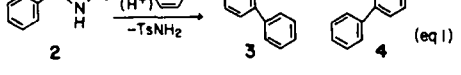
A phenoxenium ion can be represented by resonance structures, i.e. the phenyloxenium ion (**1a**), and oxocyclohexadienylium ions (**1b**, **c** and **d**). The



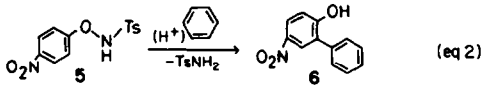
a b c d

intermediacy of the cation in chemistry and biogenesis is now supported by several lines of evidence.[1] Phenoxenium ion formation has been reported in anodic oxidation and direct chemical oxidation.[2] However, such methods cannot rule out the possible involvement of alternative or competing radical mechanisms. We recently reported the generation of phenoxenium ions through solvolysis of N-sulfonyl- and N-acyl-O-arylhydroxylamines.[3] Another method of generating the ion in solution is the thermolysis of N-aryloxypyridinium salts, where pyridine is the leaving group from the oxygen atom.[4] It is of interest to clarify whether the intermediates formed through the solvolysis and the thermolysis are common or not. In this study, the identity of the intermediates in both the reactions was verified by product analyses.

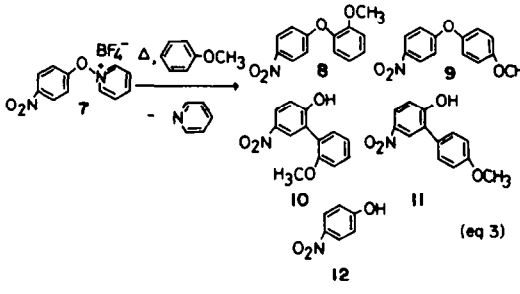
N-Tosyl-O-phenylhydroxylamine (**2**) reacts with benzene in the presence of an acid ($H_0 = -3$ to -4) to give 2-hydroxybiphenyl (**3**) and 4-hydroxybiphenyl (**4**),



2 3 4 (eq 1)



5 6 (eq 2)



7 8 9 10 11 12 (eq 3)

where the leaving group is tosylamide and benzene is the nucleophile (Eq. 1).[3] No special substituent on the phenyl ring is required and nucleophiles other than benzene, such as O- and N-nucleophiles, can be introduced on the benzene ring. This reaction is not affected by light, radical initiators or scavengers, or heavy atom-containing molecules such as carbon tetrachloride or hexabromobenzene. No diphenylether or phenol was detected by vapor phase chromatography. N-Tysol-O-(4-nitrophenyl)-hydroxylamine (**5**) reacted with benzene in the presence of an acid to give only 2-hydroxy-5-nitrobiphenyl (**6**) (Eq. 2),[3] while the 4-nitrophenoxypyridinium salt (**7**) reacted with anisole at 180° to give a mixture of 2- (**8**) and 4-methoxy-4'-nitrodiphenylether (**9**), 2-hydroxy-2'- (**10**) and 2-hydroxy-4'-methoxy-5-nitrobiphenyl (**11**), and *p*-nitrophenol (**12**) (Ed. 3).[4a,b] The most noteworthy feature is the formation of diphenylethers (**8** and **9**) in the thermolysis reaction. This raised the question of whether or not the intermediates in both the reactions are the same, and prompted us to study these reactions comparatively.

We tried to obtain the unsubstituted phenoxenium ion (**1**) from a pyridinium compound, N-phenoxy-4-methoxypyridinium salt (**13**), since, at the time this work was in progress, the electron-withdrawing substituent, NO_2, was claimed to be required for the reaction with the activated aromatic, anisole.[3a] The compound **13** was prepared from diphenyliodonium salt and 4-methoxypyridine-1-oxide, which is more nucleophilic than pyridine oxide. The pyridinium salt **13** reacted with benzene at 130° to give the expected hydroxybiphenyls **3** and **4** in 7 and 4% yields, respectively. No diphenylether was detected. Addition of trifluoroacetic acid to the thermolysis suspension in benzene somewhat improved the yields of **3** and **4** to 14 and 7%, respectively. Though the yields were low, this confirmed that benzene can be a nucleophilic aromatic compound in the thermolytic reaction as well as in the solvolysis reaction, and the presence of an electron-withdrawing group on the phenyl ring is not necessary for the reaction with aromatic compounds. Another important observation is that the *o*/*p* yield ratio in the reaction was close to 2 : *ortho* substitution characteristically predominates. A yield ratio of 2 is commonly observed in the solvolysis products of various N-sulfonyl- and N-acyl-O-phenylhydroxylamines in benzene.

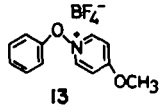
Table 1. Yields and isomer ratios of products in the reactions of 2, other N-Acyl-O-phenylhydroxylamines and 13 in benzene

Reactant	% biphenyls	3:4	% diphenylether	% phenol
PhONHTs (2)	49	67:33	0	0
PhONHCOCF$_3$*	32	69:31	0	0
PhONHCOC$_6$H$_5$†	24	63:37	0	0
PhO-$\overset{+}{P}$yr(OCH$_3$) (13)	11	64:36	0	0

* Reaction conditions: 50 equiv. of TFA, 5 equiv. of TFSA and 50 equiv. of benzene at room temperature for 2 hr.

† Reaction conditions: 50 equiv. of TFSA and 50 equiv. of benzene at room temperature for 1 hr.

The reaction of 13 with anisole was carried out under thermal conditions (reflux for 3 hr). Four biphenyl isomers, 2-hydroxy-2'-methoxy- (14, 11%), 2-hydroxy-4'-methoxy- (15, 11%), 4-hydroxy-2'-methoxy- (16, 14%) and 4-hydroxy-4'-methoxybiphenyl (17, 14%) were obtained. Diphenylethers (18) and phenol were not detected. A similar result was reported by Abramovitch *et al.*: they also did not detect 18 or phenol. The yield ratio of 14/15/16/17, 22:22:28:28 (Abramovitch reported the ratio 29:22:27:18), is in reasonable agreement with the ratio 22:27:23:28 obtained for the solvolysis of 2 in anisole.[3b] The discrepancies may be within the limits of experimental error, because the thermolysis is a heterogeneous reaction and the reaction temperatures are very different. In addition, diphenylethers and phenol are absent in both reactions. The thermolysis products ratio is not affected by the presence of added trifluoroacetic acid.



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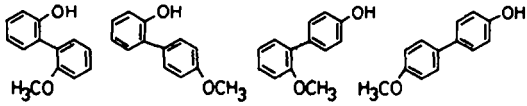
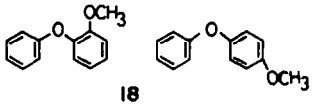


14 15 16 17



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Next, we examined the *p*-nitrophenoxenium ion. N-Tosyl-O-(4-nitrophenyl)hydroxylamine (5) reacted with benzene in the presence of trifluoroacetic acid (TFA)-trifluoromethanesulfonic acid (TFSA) at room temperature to yield 6 in 65% yield, as reported previously. In this reaction, a very small amount (less than 0.1%) of 4-nitrodiphenylether (19) was detected by VPC. N,N-Ditosyl-O-(4-nitrophenyl)hydroxylamine (20) also reacted with benzene to yield 65% of 6 and a small amount of 19 (less than 0.1%). In both cases, 4-nitrophenol 12 was not detected. 4-Nitrophenoxypyridinium salt (7) reacted with benzene at 160° for 20 hr to yield 6 (21%), and a trace of 19 (less than 0.1%), as well as an appreciable amount of 4-nitrophenol (12, 28%).

The situation was very different when the aromatic solvent was replaced with anisole (Table 4). Compound

Table 2. Yields and isomer ratios of products in the reactions of 2 and 13 in anisole

Reactant	% biphenyls	14:15:16:17	% diphenylethers	% phenol
PhONHTs (2)	64	22:27:23:28	0	0
PhO$\overset{+}{P}$yr(OCH$_3$) (13)	50	22:22:28:28	0	0

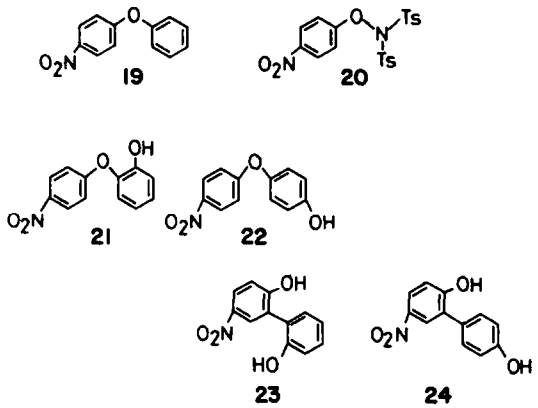
Table 3. Yields of products in the reactions of 5, 20 and 7 in benzene

Reactant	% biphenyl (6)	% diphenylether (19)	% 4-nitrophenol
NO$_2$PhONHTs (5)	65	< 0.1	0
NO$_2$PhON(Ts)$_2$ (20)	65	< 0.1	0
NO$_2$PhO$\overset{+}{P}$yr (7)	21	< 0.1	28

Table 4. Yields and isomer ratios of products in the reactions of 5, 20 and 7 in anisole

Reactant	% diphenylethers (8:9)	% biphenyls (10:11)	(8+9)/(10+11)	% 4-nitrophenol
NO$_2$PhONHTs (5)	9 (25:75)	38 (50:50)	1:4	15
NO$_2$PhON(Ts)$_2$ (20)	10 (25:75)	39 (49:51)	1:4	27
NO$_2$PhO$\overset{+}{P}$yr (7)	20 (25:75)	18 (50:50)	1:1	23

5 reacted in anisole in the presence of TFA—TFSA at room temperature to give diphenylethers **8** and **9** (9%, in a ratio of 1:3), biphenyls **10** and **11** (38%, the ratio of **10**/**11** was 1:1), and 4-nitrophenol (15%). Compound **20** under similar conditions gave **8** and **9** (10%, **8**/**9** = 1:3), **10** and **11** (39%, **10**/**11** = 1:1), and 4-nitrophenol (27%). The ratio of diphenylethers (**8** + **9**) and hydroxybiphenyls (**10** + **11**) was 4:1. The thermolysis of **7** in anisole gave **8** and **9** (20%, 1:3), **10** and **11** (18%, **10**/**11** = 1:1) and 4-nitrophenol (23%). In this case, the ratio of (**8** + **9**) and (**10** + **11**) was about 1:1. The thermolysis of **7** in phenol at refluxing temperature gave 2'-hydroxy-4-nitro- (**21**, 12%) and 4'-hydroxy-4-nitrodiphenylether (**22**, 25%), 2,2'-dihydroxy- (**23**, 17%) and 2,4'-dihydroxy-5-nitrobiphenyl (**24**, 17%), and 4-nitrophenol (24%).

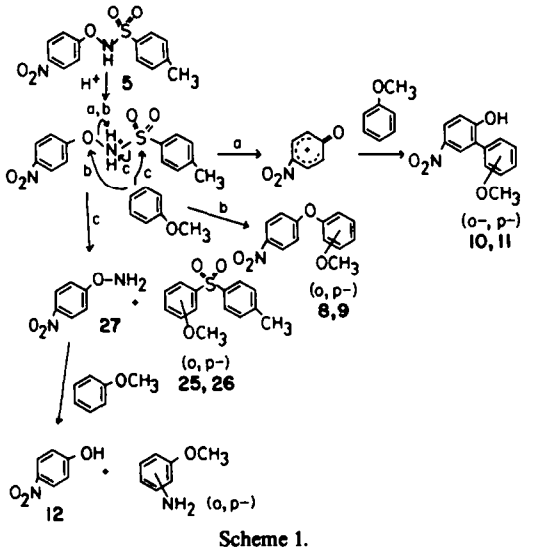


The results can be summarized as follows: (1) the *o*/*p* yield ratios of hydroxybiphenyls are the same both in the thermolysis and in the solvolysis. (2) The presence of the nitro function on the phenyl ring increased the yields of diphenylethers. (3) In benzene, diphenylethers were not formed or were formed only in a trace amount. Aromatic solvents, anisole and phenol, increased the yields of the diphenylethers. (4) The yield ratios of total diphenylethers to total hydroxybiphenyls were different in the two reactions.

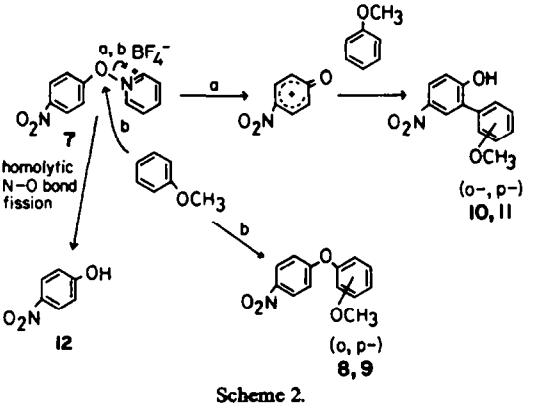
The finding that the yield ratios of the isomeric hydroxybiphenyls are always equal within experimental error strongly supports the presence of common intermediates, phenoxenium ion and 4-nitrophenoxenium ion, for the formation of hydroxybiphenyls in solvolysis and thermolysis.

Secondly, the formation of the diphenylethers occurs by a different pathway from the formation of the phenoxenium ions. The concept[4a] that nitro substitution may concentrate the positive charge on the O atom of the intermediate ion, and therefore enhance the reaction at the O atom, cannot account for the effect of nucleophilicity of the solvent, and is incompatible with the result (4) above.

The triplet phenoxenium ion pathway for the formation of diphenylethers also seems to be ruled out because this interpretation also means a common intermediate mechanism to the formation of hydroxybiphenyls. Since the radical pathway involving the phenoxy radical has been eliminated in the thermolysis[4] and no homolytic nature has been observed in the solvolysis of **2**,[3] the radical mechanism for the formation of diphenylethers is unlikely. Diphenylethers were only formed when the solvents were more nucleophilic than benzene: the more nucleophilic aromatic solvents presumably attack the oxygen atom in a concerted manner when the N—O bond cleavage is slow because of the presence of a nitro group on the phenyl ring. Then the competing pathway, the bimolecular pathway (an S_N2-like reaction at the oxygen atom) becomes predominant to give the diphenylethers.

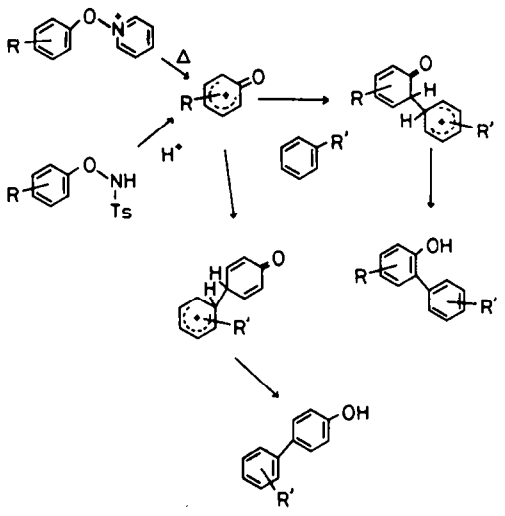


Scheme 1.



Scheme 2.

Concerning the formation of 4-nitrophenol in the solvolysis reaction, the isolation of neutral products, 2'-methoxy-4-methyl- (**25**) and 4'-methoxy-4-methyldiphenylsulfone (**26**), suggested the presence of another reaction pathway: anisole may attack the S atom in addition to the O atom when the heterolytic cleavage of the N—O bond is slow. This reaction must yield O-(4-nitrophenyl)hydroxylamine (**27**). Compound **27** could not be isolated, because it would react with anisole under the acidic conditions to yield 4-nitrophenol and anisidines. In the sovolytic reaction, *p*-anisidine was detected, though the yield was low. Benzene is not nucleophilic enough to attack the S atom as well as the O atom. Consequently, the reaction of **5** and **7** in anisole can be summarized as shown in Schemes 1 and 2. The mechanism of formation of 4-nitrophenol in the thermolysis is not yet clear. However, the pathway to 4-nitrophenol in the thermolysis must be different from that in the case of the solvolysis, and the homolytic pathway seems probable for the formation of 4-nitrophenol in thermolysis. In this case, 4-nitrophenol is also produced in benzene.



Scheme 3.

In conclusion, phenoxenium ion and 4-nitrophenoxenium ion are generated in both the thermolysis and the solvolysis, and exist as discrete species. Both ions react with benzenes to give hydroxybiphenyls, but not diphenylethers. The formation and reaction of a phenoxenium ion are represented in Scheme 3. Diphenylethers are produced by a concerted attack of more nucleophilic aromatics on the O atom. These results do not conflict with the observation of Waters:[2] phenoxenium ion reacts with phenol to give predominantly biphenyls. New and improved methods of formation of phenoxenium ions may be developed in the light of the mechanism shown in Schemes 1–3.

EXPERIMENTAL

M.ps were obtained on a Yanagimoto micro hot stage and are uncorrected. NMR spectra were determined with a JEOL JMN-FX-100 spectrometer in the solvent stated, with TMS as an internal reference. IR spectra were taken on a JASCO/D-S-402G spectrophotometer; the spectra were obtained from solid suspensions in KBr. Column chromatography was performed on silica gel (Wakogel C-200). GLC analysis was carried out on a Shimadzu GC-6A gas chromatograph using silicon OV-17 on Chromosorb W. HPLC analysis were carried out on a Shimadzu LC-3A apparatus equipped with an SPD-2A UV spectrophotometer as a detector.

4-Methoxy-1-phenoxypyridinium tetrafluoroborate (**13**). A soln of diphenyliodonium tetrafluoroborate (1.34 g) and 4-methoxypyridine-1-oxide (0.46 g) in acetonitrile (10 ml) was heated at 65° for 2 hr. Evaporation of the acetonitrile provided **13** in a quantitative yield. Recrystallization from MeOH gave colorless prisms (0.79 g), m.p. 122.5–123.5°. NMR (CD_3CN): 4.16 (3H, s), 7.04 (2H, dd, J = 8, 1.5 Hz), 7.33–7.54 (3H, m), 7.52 (2H, d, J = 7 Hz), 8.79 (2H, d, J = 7 Hz). Mass: 201 ($M^+ - HBF_4$).

Thermolysis of 4-methoxy-1-phenoxypyridinium tetrafluoroborate (**13**) *in benzene*. Powdered **13** (289 mg, 1 mmol) was suspended in benzene (13.2 ml, 150 mmol), and the mixture was heated at 130° for 24 hr in a sealed tube. The mixture was diluted with water, and extracted with CH_2Cl_2. The dried (Na_2SO_4) extract was evaporated, and the residue was chromatographed on silica gel with CH_2Cl_2 as the eluent to give 2-(**3**) and 4-hydroxybiphenyl (**4**); these products were identical with authentic samples. Quantitative analysis was carried out on the mixture, using a 1.0 m × 3 mm column of 1.5% OV-17 on Chromosorb W, with fluorene as the internal standard. Gas chromatographic yields of 2- and 4-hydroxybiphenyl were 7% and 4%, respectively. No phenol or diphenyl ether was detected.

Thermolysis of **13** *in anisole*. A mixture of **13** (289 mg, 1 mmol) and anisole (10.8 g, 100 mmol) was heated under reflux for 3 hr under an Ar atmosphere. The excess anisole was evaporated off at 55° under reduced pressure and the residue was diluted with water, then extracted with CH_2Cl_2. The dried (Na_2SO_4) extract was evaporated, and the residue was chromatographed on silica gel then purified by fractional recrystallization to yield (a) **14**, (b) **15**, (c) **16** and (d) **17**. All these products were identical with authentic samples.[3b] Quantitative analysis was carried out by GLC (1.0 m × 3 mm column; 1.5% OV-17 on Chromosorb W) using *o*-terphenyl and 4,4'-dihydroxybiphenyl as internal standards. The yields of the hydroxymethoxybiphenyls (**14**, **15**, **16** and **17**) were 11%, 11%, 14% and 14%, respectively. No phenol or methoxydiphenylethers (**18**) was detected.

Acid-catalyzed solvolysis of O-(4-nitrophenyl)-N-tosylhydroxylamine (**5**) *in benzene*. A soln of 308 mg (1 mmol) of **5** in 8.8 ml (100 mmol) of benzene was mixed with 3.8 ml (50 mmol) of trifluoroacetic acid (TFA) and 0.88 ml (10 mmol) of trifluoromethanesulfonic acid (TFSA) and the whole was stirred for 20 hr at room temp. The mixture was diluted with water, then neutralized with $NaHCO_3$ aq, and extracted with CH_2Cl_2. The extract was dried over Na_2SO_4, filtered and concentrated. The crude product was purified by silica gel column chromatography to give **6**: pale yellow needles, m.p. 124–125° (lit[3b] m.p. 124–125°). A trace amount of **19** was isolated by p-TLC on silica gel with CH_2Cl_2 hexane (1:2): pale yellow needles, m.p. 52–53°. The products were identical with authentic samples. Quantitative analysis was carried out on the crude product using a 0.5 m × 3 mm column of 3% OV-17 on Chromosorb W, with 2-hydroxy-2'-methoxy-5-nitrobiphenyl as an internal standard. The yield of **6** was 65%, and the yield of **19** was less than 0.1%.

Acid-catalyzed solvolysis of O-(4-nitrophenyl)-N,N-ditosylhydroxylamine (**20**) *in benzene*. The procedure and the quantitative analysis were the same as those for the solvolysis of **5** with benzene: 462 mg of **20**, 8.8 ml of benzene, 3.8 ml of TFA and 0.8 ml of TFSA were used. The yields of products (**6** and **19**) were 65% and less than 0.1%, respectively.

Thermolysis of N-(4-nitrophenoxy)pyridinium tetrafluoroborate (**7**) *in benzene*. Powdered **7** (304 mg, 1 mmol) was suspended in benzene (8.8 ml, 100 mmol), and the mixture was heated at 160° for 20 hr in a sealed tube. The mixture was diluted with CH_2Cl_2 and washed with water. The dried (Na_2SO_4) organic layer was filtered and the filtrate was evaporated to give a residue. Quantitative analysis was carried out by the same method as that for the solvolysis of **5** with benzene. The yields of products (**6** and **19**) were 21% and less than 0.1%, respectively.

Acid-catalyzed solvolysis of O-(4-nitrophenyl)-N-tosylhydroxylamine (**5**) *in anisole*. TFA (3.8 ml, 50 mmol) and TFSA (2.2 ml, 25 mmol) were added to a soln of **5** (308 mg, 1 mmol) in 10.8 g (100 mmol) of anisole with stirring at room temp. After 20 hr, the mixture was diluted with water. The whole was neutralized with $NaHCO_3$ aq followed by extraction with CH_2Cl_2. The extract was dried over Na_2SO_4 and filtered. The solvent was evaporated off under reduced pressure at 55°. The crude product was chromatographed on a column of silica gel, and the following compounds were isolated. (a) A mixture of **8** and **9**; the products were isolated by fractional recrystallization from hexane. 2-Methoxy-4'-nitrodiphenylether: pale yellow needles, m.p. 102–103° (lit[4c] m.p. 104–105°); NMR ($CDCl_3$): δ 3.79 (s, 3H), 6.88–7.36 (m, 6H), 8.17 (d, 2H, J = 9 Hz). 4-Methoxy-4'-nitrodiphenylether: pale yellow needles, m.p. 110–111° (lit[4c] m.p. 111°); NMR ($CDCl_3$): δ 3.84 (s, 3H), 6.84–7.28 (m, 6H), 8.16 (d, 2H, J = 9 Hz). (b) Compound **10**: pale yellow needles, m.p. 133–134° (lit[4c] m.p. 133–135°); NMR ($CDCl_3$): δ4.10 (s, 3H), 6.94 (s, 1H), 7.13–7.78 (m, 5H), 8.24–8.49 (m, 2H). (c) Compound **11**: yellow needles m.p. 145° (lit[4c] m.p. 145°); NMR ($CDCl_3$): δ 4.02 (s, 3H), 6.20 (s, 1H), 7.10 (m, 3H), 7.58 (d, 2H, J = 9 Hz), 8.16–8.36 (m, 2H). (d) Compound **12**: slightly yellow needles, m.p. 113–114°. Quantitative analysis

was carried out on the diphenylethers and hydroxybiphenyls after rough separation by silica gel chromatography using CH_2Cl_2 to give a mixture of **8** and **9**, and a mixture of **10**, **11** and **12**. Gas chromatographic analysis was carried out using a 0.5 m × 5 mm column of 3% OV-17 on Chromosorb W. The diphenylethers were separated at a column temp of 180° using 2-hydroxy-5-nitrobiphenyl as an internal standard. The hydroxybiphenyls were separated at 200° using 4-methoxy-4'-nitrodiphenylether as an internal standard. Analysis of 4-nitrophenol was carried out by using the same column at 127° with *m*-dinitrobenzene as an internal standard. The yields of the products (**8**, **9**, **10**, **11** and **12**) were 2.3, 6.9, 19, 19 and 15%, respectively. A mixture of **25** and **26** was obtained as a less polar fraction when the mixture was chromatographed on silica gel with CH_2Cl_2–n-hexane (2:1) as an eluent. The mixture of **25** and **26** was chromatographed on a silica gel column with EtOAc–n-hexane (1:3) as an eluent to give **25** and **26** in 6% and 6% yields, respectively. Compound **25**: colorless needles, m.p. 84–85°; NMR ($CDCl_3$): δ 2.40 (s, 3H), 3.96 (s, 3H), 6.95–7.70 (m, 4H), 6.93 (d, 2H, J = 6 Hz), 7.77 (d, 2H, J = 6 Hz). (Found: C, 63.81; H, 5.31. Calc for $C_{14}H_{14}O_3S$: C, 64.09; H, 5.38%.) Compound **26**: colorless needles, m.p. 101–103° (lit[5] m.p. 102.5–104°); NMR ($CDCl_3$): δ 2.38 (s, 3H), 3.83 (s, 3H), 6.92 (d, 2H, J = 6 Hz), 7.24 (d, 2H, J = 6 Hz), 7.76 (d, 2H, J = 6 Hz), 7.84 (d, 2H, J = 6 Hz). (Found: C, 63.90; H, 5.36. Calc for $C_{14}H_{14}O_3S$: C, 64.09; H, 5.38%.) Compounds **25** and **26** were identified by comparison of their IR spectra with those of authentic samples. The authentic samples were prepared by Friedel–Crafts sulfonylation of anisole with *p*-toluenesulfonyl chloride. 2-Anisidine and 4-anisidine were detected by GLC in yields of less than 1%.

Acid-catalyzed solvolysis of O-(*4-nitrophenyl*)-N,N-*ditosylhydroxylamine* (**20**) *with anisole.* The procedure and the quantitative analysis were the same as those for the solvolysis of 7 with anisole: 462 mg of **20**, 10.8 g of anisole, 3.8 ml of TFA and 2.2 ml of TFSA were used. The yields of products (**8**, **9**, **10**, **11** and **12**) were 2.5, 7.5, 19, 20 and 27%, respectively.

Decomposition of O-(*4-nitrophenyl*)*hydroxylamine* (**27**) *in anisole in the presence of acids.* A mixture of 154 mg (1 mmol) of **27**, 10.8 g (100 mmol) of anisole, 3.8 ml (50 mmol) of TFA and 2.2 ml (25 mmol) of TFSA was heated at 35–40° for 20 hr. The mixture was diluted with water and neutralized with $NaHCO_3$ aq followed by extraction with CH_2Cl_2. The extract was dried over Na_2SO_4 and filtered. The solvent was evaporated off under reduced pressure at 55°. The residue was chromatographed on silica gel to give **12** 49%, 2-anisidine 2.5% and 4-anisidine 2.5%; these products were identical with authentic samples.

Thermolysis of 1-(*4-nitrophenoxy*)-*pyridinium tetrafluoroborate* (**7**) *in anisole.* A mixture of **7** (304 mg, 1 mmol) and anisole (10.8 g, 100 mmol) was heated under reflux for 5 hr under an Ar atmosphere. The mixture was dissolved in CH_2Cl_2 and the whole was washed with water. The organic layer was dried over Na_2SO_4 and filtered. The solvent was evaporated off under reduced pressure at 55° to give a brownish residue. The method of quantitative analysis was the same as that for the solvolysis of **5** in anisole. Gas chromatographic yields of products (**8**, **9**, **10**, **11** and **12**) were 5, 15, 9, 9, and 23%, respectively.

Thermolysis of **7** *in phenol.* A mixture of **7** (304 mg, 1 mmol) and phenol (9.4 g, 100 mmol) was heated under reflux for 5 hr under an Ar atmosphere. Phenol was removed under a vacuum at 60°. The residue was dissolved in CH_2Cl_2 and chromatographed on a silica gel column. The following compounds were isolated. (a) Compound **21**: colorless needles, m.p. 104–105°; NMR ($CDCl_3$): δ 4.35 (s, 1H), 6.90–7.18 (m, 4H), 7.06 (d, 2H, J = 6 Hz), 8.21 (d, 2H, J = 6 Hz). (Found: C, 62.28; H, 3.87; N, 6.14. Calc for $C_{12}H_9NO_4$: C, 62.34; H, 3.92; N, 6.06%.) (b) Compound **22**: pale yellow prisms, m.p. 172–173° (lit[6] m.p. 171–172°); NMR [$(CD_3)_2SO$]: δ 6.83 (d, 2H, J = 7 Hz), 7.01 (d, 2H, J = 7 Hz), 7.06 (d, 2H, J = 6 Hz), 8.21 (d, 2H, J = 6 Hz), 9.53 (s, 1H). (Found: C, 62.06; H, 3.82; N, 6.09. Calc for $C_{12}H_9NO_4$: C, 62.34; H, 3.92; N, 6.06%.) (c) Compound **23**: pale yellow needles, m.p. 171°; NMR [$(CD_3)_2SO$]: δ 6.76–7.28 (m, 5H), 7.99–8.13 (m, 2H), 10.18 (br s, 2H). (Found: C, 62.03; H, 3.86; N, 6.09. Calc for $C_{12}H_9NO_4$: C, 62.34; H, 3.92; N, 6.06%.) (d) Compound **24**: yellow needles, m.p. 145°; NMR [$(CD_3)_2SO$]: δ 6.82 (d, 2H, J = 6 Hz); 7.00–7.11 (m, 1H), 7.42 (d, 2H, J = 6 Hz), 7.96–8.12 (m, 2H), 9.57 (br s, 2H). (Found: C, 62.27; H, 3.96; N, 6.12. Calc for $C_{12}H_9NO_4$: C, 62.34; H, 3.92; N, 6.06%.) (e) Compound **12**.

Compounds **21**, **22**, **23** and **24** were identified by comparison of their IR spectra with those of authentic samples. The authentic samples were respectively prepared from **8**, **9**, **10** and **11**, which were obtained as the products of the reaction of **5** in anisole upon treatment with BBr_3 in CH_2Cl_2 at −78°. Quantitative analysis was carried out as follows. The residual mixture was roughly chromatographed on silica gel to give a mixture of **21** and **22**, and a mixture of **23**, **24** and **12**. The analysis of diphenylethers was carried out by GLC (0.5 m × 5 mm column, 3% OV-17 on Chromosorb W) using 4'-methoxy-4-nitrodiphenylether as the internal standard. The yields of **21** and **22** were 12% and 25%, respectively. 4-Nitrophenol (**12**) was analyzed by GLC using the same column, with *m*-dinitrobenzene as an internal standard. The yield of **12** was 24%. The analysis of **23** and **24** was carried out by HPLC (Waters Co., Radial Pack A, reverse phase; solvent, H_2O–MeOH 6:1, containing 5% NH_4OH) using 2-hydroxy-5-nitrobiphenyl as the internal standard. The yields of **23** and **24** were 17 and 17%, respectively.

REFERENCES

[1] H. Musso, *Oxidative Coupling of Phenols* (Edited by W. I. Taylor and A. R. Battersby), Marcel Dekker, New York (1967); D. H. R. Barton, *Chem. Ber.* **3**, 330 (1967).

[2] K. Dimroth, W. Umbach and H. Thomas, *Chem. Ber.* **100**, 132 (1967); B. Speiser and A. Rieker, *J. Chem. Res.* Miniprint 3601 (1977); A. Rieker, E. L. Dreher, H. Geisel and M. H. Khalifa, *Synthesis* 851 (1978); J. W. A. Findlay, P. Gupta and J. R. Lewis, *J. Chem. Soc. C.* 2761 (1969); D. G. Hewitt, *J. Chem. Soc. C* 1750 (1971); W. A. Waters, *J. Chem. Soc. B* 2026 (1971).

[3a] Y. Endo, K. Shudo and T. Okamoto, *J. Am. Chem. Soc.* **99**, 7721 (1977); [b] Y. Endo, K. Shudo and T. Okamoto, *Ibid.* **104**, 6393 (1982).

[4a] R. A. Abramovitch, M. N. Inbasekaran and S. Kato, *J. Am. Chem. Soc.* **95**, 5428 (1973); [b] R. A. Abramovitch, G. Alvernhe and M. N. Inbasekaran, *Tetrahedron Letters* 1113 (1971); [c] R. A. Abramovitch, G. Alverhne, R. Bartnik, N. L. Dassanayake, M. N. Inbasekaran and S. Kato, *J. Am. Chem. Soc.* **103**, 4558 (1981); [d] R. A. Abramovitch and M. N. Inbasekaran, *Tetrahedron Letters* 1109 (1977).

[5] J. B. Hyne and J. W. Greidanus, *Can. J. Chem.* **47**, 803 (1969).

[6] K. Tatsumi, S. Kitamura, H. Yoshimura and Y. Kawazoe, *Chem. Pharm. Bull.* **26**, 1713 (1978).