Acid-Catalyzed Solvolysis of *N*-Sulfonyl- and *N*-Acyl-*O*-arylhydroxylamines. Phenoxenium Ions

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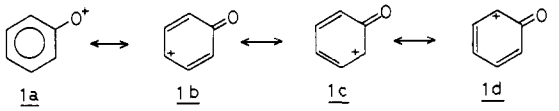
Abstract: The acid-catalyzed reaction of *N*-acyl- and *N*-sulfonyl-*O*-arylhydroxylamines with benzene proceeded quite smoothly to give 2- and 4-hydroxybiphenyls. The results of product analysis, the orientation of the reaction, and the effects of substituents on the nitrogen atom and on the phenyl ring suggested a mechanism that involves a phenoxenium ion. The phenoxenium ion was trapped by benzene and other various nucleophiles.

A phenoxenium ion can be represented by resonance tautomers, i.e., the phenyloxenium ion (**1a**) and oxocyclohexadienylium cations (**1b–d**). The intermediacy of such a cation has often been

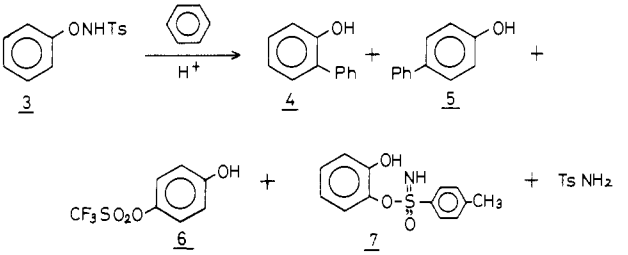


1a 1b 1c 1d

suggested in connection with biosynthetic phenolic coupling[1] and the oxidation of phenols by thallium(III),[2] chromic acid,[3] and iodine–Ag.[4] The production of phenoxenium ions has been established through anodic oxidation coupled with potential-sweep measurements.[5] Moreover, the isolation of crystalline phenoxenium ion salts has been reported, though the cation was resonance stabilized by three aryl groups.[6] Reactions involving electrophilic substitution by a phenoxenium ion into an anisole nucleus during the oxidation of certain benzophenones[7] and thermolysis of (*p*-nitrophenoxy)pyridinium salts were reported.[8] We have been seeking a general method for producing the phenoxenium ion by elimination of a nucleofugal group from an oxygen atom. We studied the elimination of the amino group from *O*-amino derivatives of phenol in connection with acid-catalyzed elimination of the hydroxyl group from *N*-phenylhydroxylamines[9] or the amino group from phenylhydrazines.[10] In this paper, the formation of phenoxenium ions, including the simplest (unsubstituted) one, and their reactions with benzene and other nucleophiles are described. Evidence for the phenoxenium ion obtained here supports the mechanism proposed for the previous reactions.[1-8] The reaction with benzene described here is general and provides a versatile synthetic method for biphenyl derivatives. Some of the present results have already been summarized in this journal.[11] Recently, 4-nitrophenoxenium ion formation by acylamino elimination and other methods was reported by Abramovitch.[12]

Results

Reactions in Benzene. Acid-catalyzed reaction of *O*-phenylhydroxylamine (**2**)[13,14] in benzene in the presence of trifluoromethanesulfonic acid (TFSA) under reflux yielded phenol and aniline. Diazotization of the amino group was attempted in benzene with nitrosyl tetrafluoroborate, but after workup the only isolated product was phenol. Thus, the amino group was modified to a sulfonylamino group, which is a better leaving group than amine. N-Tosylation of **2** with tosyl chloride in pyridine smoothly gave a stable *N*-tosyl-*O*-phenylhydroxylamine (**3**). A mixture of TFSA (2.5 equiv) and trifluoroacetic acid (TFA, 50 equiv) was added to a solution of **3** in benzene (50 equiv to **3**), and the whole was allowed to stand for 1 h at room temperature or below.



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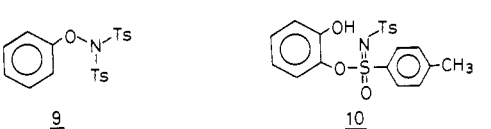
Products identified were hydroxybiphenyls (49%) [which consisted of 2- and 4-hydroxybiphenyls (**4** and **5**) in a ratio of 2:1], 4-(((trifluoromethyl)sulfonyl)oxy)phenol (**6**, 3%), and a rearranged catechol derivative, 2-hydroxyphenyl *p*-toluenesulfonimidate (**7**, 13%), for a total products yield of 65%, and *p*-toluenesulfonamide (85%). In the presence of TFA (50 equiv) alone, the reaction proceeded slowly, and the yields of **4** and **5** were low. Diphenyl ether, biphenyl, and phenol were not detected in the reaction mixture by VPC. Diphenyl ether was not isomerized to hydroxybiphenyls under these reaction conditions.

N-((Trifluoromethyl)sulfonyl)-*O*-phenylhydroxylamine (**8**) also reacted with benzene in the presence of TFSA (20 equiv) to give **4** and **5** in 20% and 11% yields, respectively. *N*,*N*-Ditosyl-*O*-phenylhydroxylamine (**9**) was another sulfonamide that reacted



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with benzene; TFA alone catalyzed the reaction at 5 °C to give **4** (20%), **5** (8%), and a rearranged product (**10**, 32%). The structure of **10** was deduced on the basis of alkaline hydrolysis of **10** to **7**.

Acylamides could be leaving groups, though in this case the intramolecular rearrangement predominates. The reaction of

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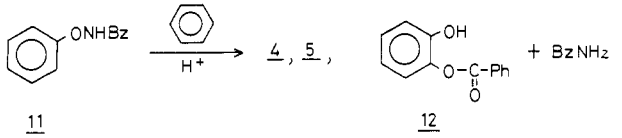
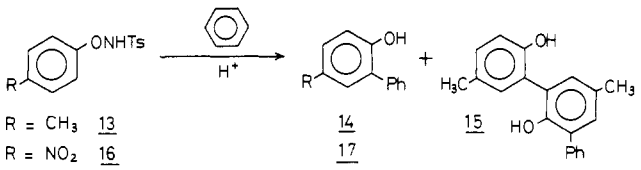
N-benzoyl-*O*-phenylhydroxylamine (**11**) in benzene (100 equiv)



in the presence of TFA (50 equiv)–TFSA (10 equiv) (abbreviated as TFA–TFSA (50:10) in the text below) for 24 h at room temperature gave **4** (6%), **5** (3%), catechol monobenzoate (**12**, 43%), and benzamide. In the absence of benzene, the major product was **12** (78%). In the presence of TFSA (30 equiv) alone, the yield of hydroxybiphenyls increased to 24%. The *N*-acetyl derivative gave hydroxybiphenyls in a poor yield (7%), but *N*-trifluoroacetamide is a better leaving group among acylamides: the yield of hydroxybiphenyls is 45% (**4**:**5** = 2:1).

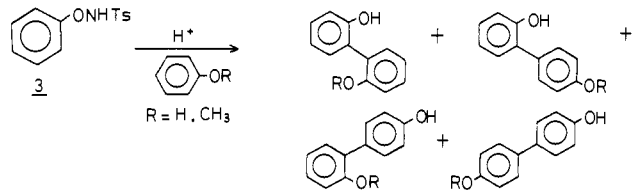
The lower yields observed for the reactions of acylamides relative to the analogous reactions of sulfonamides were due to the accompanying rearrangement to catechol derivatives. The formation of **4** and **5** appears to compete with the formation of the rearrangement products. It is noteworthy that the yield ratio of 2- and 4-hydroxybiphenyls is very close to 2, regardless of the change of sulfonyl and acyl groups.

N-Tosyl-*O*-(4-methylphenyl)hydroxylamine (**13**) is more reactive than **3**. This amide reacted with benzene in the presence of TFA alone at room temperature to give 2-hydroxy-5-methylbiphenyl (**14**, 26%), though a better yields was obtained



by the use of TFA:TFSA (50:1) at 0 °C: **14** (44%) together with a secondary product (**15**, 9%) formed from **14**. In this case no phenylation of the 4-position occurred. This is remarkably different from the acid-catalyzed reaction of *N*-(4-methylphenyl)-hydroxylamine with benzene, where the major product was formed from the attack of benzene at the para position.[9] *N*-Tosyl-*O*-(4-nitrophenyl)hydroxylamine (**16**) did not react with benzene in the presence of TFA, and the presence of TFA:TFSA (50:10) (20 h at room temperature) was required for the formation of 2-hydroxy-5-nitrobiphenyl (**17**, 41% yield).

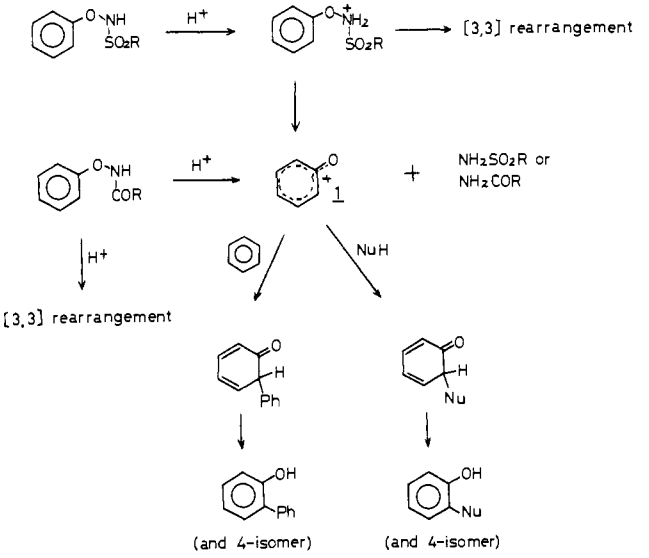
A similar reaction of the tosylate (**3**) in anisole (50 equiv) in the presence of TFA:TFSA (50:1) gave (in 65% yield) a mixture of hydroxymethoxybiphenyls that consisted of 2- (23%) and 4-hydroxy-2′-methoxybiphenyls (23%) and 2- (27%) and 4-hydroxy-4′-methoxybiphenyls (27%).



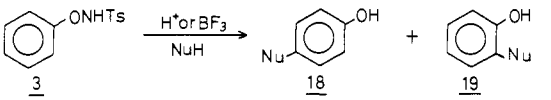
Reaction with phenol similarly gave (in 70% yield) a mixture of dihydroxybiphenyls that consisted of 2,2′- (13%), 2,4′- (47%), and 4,4′-dihydroxybiphenyls (40%). These reactions suggest that the reactive species formed from **3** is electrophilic.

Reactions in Alcohols and Other Solvents. In the reaction of **3** in benzene catalyzed by TFSA–TFA, the formation of 4-(((trifluoromethyl)sulfonyl)oxy)phenol (**6**) as a product can be interpreted in terms of trapping of an intermediate by a nucleophile, a triflate anion. This means that nucleophiles other than benzene and phenol would be introduced into the phenyl ring of **3** if the medium is acidic enough to protonate the amide and the reactive intermediate is produced. The acidity required for the reaction is $H_0 = -3.0$ to -4.0, as experimentally determined by examination of the dependence of the reaction on the acidity of the trifluoroethanol–TFSA system.[15] Thus, in TFA–TFSA (5:1)

Scheme I



without benzene, the tosylate (**3**) yielded the 4-sulfate (**6**, 20–30%), the rearranged product (**7**, 30%), and a trace of 2-sulfate (trace, less than 1%). In acetic acid (75:6 acetic acid–TFSA), the nucleophiles are triflate anion and acetic acid; the products were 4-acetoxyphenol (11%), 2-acetoxyphenol (trace, less than 1%), the sulfate (**6**, 16%), and the rearranged product (**7**, 23%). In trifluoroethanol (100:5 trifluoroethanol–TFSA), 4-(trifluoroethoxy)phenol (**18**, Nu = CF_3CH_2O–, 32%) and the 2-isomer (**19**, Nu = CF_3CH_2O–, 3%) were formed. Boron trifluoride etherate



(5 equiv) in 150 equiv of trifluoroethanol yields **18** (Nu = CF_3CH_2O–, 34%) and the 2-isomer (4%) in addition to **7**. Methanol is a more basic solvent than those mentioned above. Continuous bubbling of BF_3 gas through the methanol at 0 °C was required in order to obtain sufficient acidity for the reaction; 4-methoxyphenol (16%), 2-methoxyphenol (3%), and **7** (21%) were identified. Acetonitrile, a nitrogen nucleophile, attacked the intermediate to give 4-acetamidophenol (15%) in addition to an unidentified compound of molecular formula $C_{15}H_{16}N_2O_3S$ (55%). This reaction was catalyzed by 2.5 equiv of TFSA. A solution of **3** in ethanethiol (100 equiv) and methylene chloride was treated with BF_3 gas at 0 °C to yield 2-ethylmercaptophenol (**19**, Nu = C_2H_5S, 23%) and 4-ethylmercaptophenol (**18**, Nu = C_2H_5S, 43%). Introduction of hydrogen chloride into a TFA solution of **3** gave 4- (10%) and 2-chlorophenol (18%). These reactions can be generalized as shown in the equation **3** → **18** + **19**.

Discussion

The illustrated reactions of *N*-sulfonyl- and *N*-acyl-*O*-phenylhydroxylamines represent acid-catalyzed solvolyses with elimination of a sulfonamide or an acylamide moiety from a phenyl-substituted oxygen atom. The mechanism in Scheme I accommodates all the observations. The sulfonamide (or acylamide) is protonated, and the heterolytic O–N bond cleavage generates a delocalized phenoxenium ion (**1**), whose cationic charge is largely located on the phenyl ring. The ion is trapped by nucleophiles such as benzene, anisole, phenol, triflate anion, trifluoroethanol, acetic acid, thiol, alcohol, and acetonitrile in the solvent. Thus, 2- and 4-substituted phenols are produced. A very similar scheme has been proposed for 4-nitrophenoxenium ion by Abramovitch in the thermolytic reaction of (*p*-nitrophenoxy)-pyridinium salt.[8] The position of protonation leading to the formation of **1** may be the nitrogen atom (sulfonamide) and the

(15) The H_0 acidity function for the TFSA–trifluoroethanol system will be reported elsewhere.

oxygen atom (acyl amide) on the basis of an NMR study of amide protonations.[16,17] Either N-protonation or O-protonation increases the leaving ability of the amide groups.

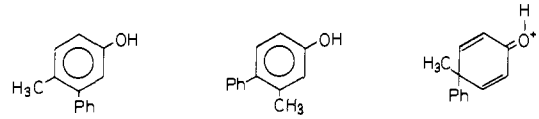
Tosylamide is one of the best leaving groups from the oxygen atom. A better leaving group, *N,N*-ditosylamide, could be eliminated more easily by a weak acid. The reaction does not necessarily require an acid that is of high acidity, but a stronger acid is preferable for elimination of a poorer leaving group. The effect of 4-substitution of the O-aryl group on the reaction rate indicates that the cleavage of the N–O bond depends on the electron-releasing power of the substituents. The nitro substitution requires more severe conditions, compatible with the formation of an electron-deficient species. In the reaction in anisole and phenol, the product compositions clearly indicate that the reactive species is electrophilic: the ortho and para positions of phenol and of anisole are attacked.

It is very significant that, regardless of the leaving power of several different amide groups, the yield ratio (*o*/2*p*) of 2- and 4-hydroxybiphenyls, the products obtained by trapping with benzene, is always approximately 1.0. This strongly suggests that all the amides yield a common reactive intermediate in the rate-determining step of each reaction. This is evidence against the pathway via a concerted nucleophilic attack of benzene in an S_N2 manner. A significant difference in the *o*/2*p* ratio should be observed if the attack of benzene is concerted with the elimination of the amide group, because the steric and electronic differences of the leaving groups would still be expected to be present at the transition state of the reaction.

The yield of 4-(((trifluoromethyl)sulfonyl)oxy)phenol (**6**) was higher in the medium where the only nucleophile other than benzene is the sulfate anion: this provides strong evidence for the ionic mechanism. Radical initiators or scavengers had no effect on the reaction, and no possible products formed by a radical process were detected; these observations also eliminate a possible homolytic mechanism. The isolation of **6** suggested that if other nucleophiles were present, the reactive intermediate would be trapped by them. This was proved when the reaction was conducted under conditions of sufficient acidity (about $H_0 = -3$ to -4) to effect the substantial protonation of amide groups and in the presence of a nucleophilic solvent in place of benzene. Since trifluoromethanesulfate anion was always present, **6** was one of the products in each reaction when TFSA was used. Various oxygen and nitrogen nucleophiles were captured, though the kinds of nucleophilic species available under these acidic conditions are limited. Chlorine was introduced in the same manner. The presence of hydrogen bromide and iodide yielded bromo- and iodophenols, respectively, but these should be largely formed by halogenation of phenol with bromine and iodine (**3** oxidizes hydrogen bromide and iodide to bromine and iodine, with the formation of phenol).

A noteworthy result is the significant change of ratios of 2- and 4-substitutions with different nucleophiles. The *o*/2*p* ratio is 1–1.1 for benzene, 0.3 for thiol, less than 0.1 for oxygen nucleophiles, methanol and trifluoroethanol, 0.9 for chloride, and less than 0.1 for triflate and acetic acid. The marked changes in the ratio seem to be correlated with the HOMO orbital energies of nucleophiles. Softer nucleophiles such as benzene and thiol give more ortho products, and harder nucleophiles such as trifluoroethanol give more para products. The orbital nature of the phenoxenium ion is open to debate.

Participation of a protonated species of **1** in the reaction seems to be rather unlikely because a strong acid is not necessarily required for the reaction; TFA is strong enough to cause the reaction if the leaving group is good. It was reported that the electrochemically formed diaryloxenium ion is not protonated in TFA.[18] Triphenylphenoxenium ions are not protonated in 60% perchloric acid.[6] In addition, the reaction of *O*-(4-methylphenyl)-*N*-tosylhydroxylamine (**13**) did not yield compounds **20** and **21**, derived from **22** formed by the initial attack of benzene



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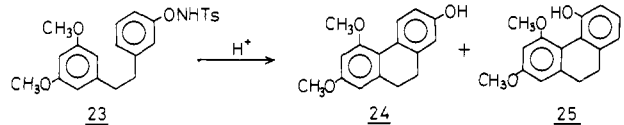
at the para position; on the contrary, *N*-(4-methylphenyl)-hydroxylamine reacts with benzene predominantly at the para position, where participation of a protonated anilenium ion is rigorously established.[9]

The phenoxenium ion produced from several *O*-amides reacts with benzene on the aromatic ring, not on the oxygen atom. This would be anticipated on the basis of electronegativities: the oxygen atom should be much less able to bear a positive charge than carbon atoms. The phenoxenium ion bearing a *p*-nitro group generated from the tosylamide (**16**) also did not react at its oxygen atom with benzene. This is in remarkable contrast with the result reported for the *p*-nitrophenoxenium ion proposed by Abramovitch, which, on reaction with anisole, yielded 4-nitro-4′-methoxydiphenyl ether and hydroxybiphenyls.[8] This difference may be attributed at least partly to the higher reaction temperature in the pyrolytic reaction, where regioselectivity is poorer than in low-temperature solvolysis. The thermolysis is always accompanied by the formation of *p*-nitrophenol via a homolytic pathway or a triplet phenoxenium ion, Ar–Ȯ·⁺, while the present solvolytic reaction does not produce phenols. Therefore, another possible interpretation of the difference is that the diphenyl ether is formed through the triplet intermediate (or a radical), while the biphenyls are formed through the singlet phenoxenium ion; the solvolysis yields only the singlet phenoxenium ion.

The formation of the rearranged products (**7**, **10**, and **12**) can reasonably be explained by acid-catalyzed [3,3]-sigmatropic-like rearrangement, which competes with the formation of the free phenoxenium ion. This is a useful synthetic method for catechol derivatives.[14]

Conclusion

The acid-catalyzed solvolytic reaction of *O*-aryl-*N*-sulfonyl- and *O*-aryl-*N*-acyl-hydroxylamines has been described. The initial formation of a highly delocalized phenoxenium ion (**1**) and subsequent reactions with solvents give ring-substituted phenols. The phenoxenium ion reacts with benzene, phenol, thiol, and other nucleophilic solvents to yield 2- and 4-substituted phenols. The reaction with benzene is of synthetic use. An application can be seen in the synthesis of orchinol (**24**) and loroglossol (**25**)[19] (through intramolecular cyclization of **23**) and of other di-



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hydrophenanthrenes.[20] This, as well as the reaction with phenol, suggests the possibility of participation of a phenoxenium ion in the biosynthesis of diaryls.[1] The reaction presented here seems to be of some importance in the field of aromatic chemistry, and the results are of both practical and theoretical interest.

Experimental Section

Melting points were obtained on a Yanagimoto micro hot stage and are uncorrected. NMR spectra were determined with a JEOL JMN-PS-100 spectrometer in the solvent stated with tetramethylsilane as an internal reference. IR spectra were obtained on a JASCO D-S-402G spectrophotometer; the spectra were recorded in the solvent stated, neat or as a solid suspension in KBr. Mass spectra were taken on a JEOL

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MS-SG-01 mass spectrometer. All spectra for new compounds were consistent with their assigned structures. Column chromatography was performed on silica gel (Wakogel C-200) with methylene chloride or methylene chloride–hexane as the eluent. Gas chromatography was performed by using silicone OV-17 (1.5% or 3%) on Chromosorb W, unless otherwise noted. Microanalyses were carried out in the microanalytical laboratory of this faculty.

Preparation of *O*-Arylhydroxylamines. *O*-Phenyl and *O*-4-tolylhydroxylamines were prepared following the general procedure reported in the previous paper[14] or the method described by Bumgardner and Lilly.[13] *O*-(4-Nitrophenyl)hydroxylamine was prepared from 4-nitrofluorobenzene (7.0 g in 100 mL of anhydrous ethanol), potassium hydroxide (3.10 g), and ethyl acetohydroxamate (5.11 g in 50 mL of anhydrous ethanol) under ice cooling. After being allowed to stand for 6 h at room temperature, the reaction mixture was poured into ice–water. Pale yellow precipitates were filtered off and crystallized from *n*-hexane to give ethyl *O*-(4-nitrophenyl)acetohydroxamate as colorless plates (5.9 g, 53%). TFSA (10 mL) was added to a solution of ethyl *O*-(4-nitrophenyl)acetohydroxamate (3.56 g) in 50 mL of dioxane and 5 mL of water with stirring at below 10 °C over 10 min. The reaction mixture was stirred for 4 h at room temperature, and then poured into ice–water to give a yellow solid, which was filtered off and washed with water. Crystallization from methylene chloride–*n*-hexane afforded pale yellow needles (1.03 g, 41%) of *O*-(4-nitrophenyl)hydroxylamine; mp 126–127 °C. Anal. ($C_6H_6N_2O_3$): C, H, N.

***O*-Aryl-*N*-(*p*-toluenesulfonyl)hydroxylamines (3, 13, and 16). General Procedure**: N-Tosylation of *O*-arylhydroxylamine (10 mmol) with tosyl chloride (12 mmol) in pyridine (20 mL) at room temperature gave the product (**3**, **13**, or **16**) in 75–85% yield. *O*-Phenyl-*N*-tosylhydroxylamine (**3**): colorless needles; mp 113–114 °C (chloroform–*n*-hexane). Anal. ($C_{13}H_{13}NO_3S$): C, H, N. *O*-4-Tolyl-*N*-tosylhydroxylamine (**13**): colorless needles; mp 114–116 °C (chloroform–*n*-hexane). Anal. ($C_{14}H_{15}NO_3S$): C, H, N. *O*-(4-Nitrophenyl)-*N*-tosylhydroxylamine (**16**): colorless needles; mp 178–180 °C (from benzene). Anal. ($C_{13}H_{12}N_2O_5S$): C, H, N.

Acid-Catalyzed Reaction of 3 with Benzene. A mixture of TFSA (0.44 mL, 5 mmol) and 7.6 mL (50 mmol) of trifluoroacetic acid was added to a solution of **3** (526 mg, 2 mmol) in 8.8 mL (50 mmol) of benzene with stirring at 5 °C. The resulting solution was allowed to stand at room temperature for 1 h. The mixture was diluted with water, then neutralized with aqueous sodium hydrogen carbonate, and extracted with methylene chloride. The extract was dried over anhydrous sodium sulfate, filtered, and concentrated. The crude product was chromatographed on silica gel with methylene chloride as the eluent, and the following compounds were isolated. (a) 2-Hydroxybiphenyl (**4**): 99 mg (29%); colorless needles (from *n*-hexane); mp 56–57 °C. (b) 4-Hydroxybiphenyl (**5**): 48 mg (14%); colorless plates (from benzene); mp 166–167 °C. (c) 4-(((Trifluoromethyl)sulfonyl)oxy)phenol (**6**): 15 mg (3%); colorless viscous liquid; this product was identified by comparison with an authentic sample prepared from hydroquinone and trifluoromethanesulfonic anhydride. (d) 2-Hydroxyphenyl *p*-toluenesulfonimidate (**7**): 68 mg (13%); pale brown leaflets (from methylene chloride–*n*-hexane); mp 125 °C. Anal. ($C_{13}H_{13}NO_3S$): C, H, N. (e) *p*-Toluenesulfonamide: 291 mg (85%); colorless needles (from methylene chloride–*n*-hexane) mp 138–140 °C; this product was identified by comparison of its IR spectrum with that of an authentic sample. Gas chromatographic yields of 2- and 4-hydroxybiphenyl were 33% and 16%, respectively.

***O*-Phenyl-*N*-((trifluoromethyl)sulfonyl)hydroxylamine (8).** Trifluoromethanesulfonic anhydride (4.19 g) was added to a solution of **2** (2.945 g) in 25 mL of benzene with stirring at 0 °C. The mixture was allowed to stand for 1 h. Precipitates (TFSA salt of **2**) were filtered off, and the filtrate was concentrated at room temperature under reduced pressure. Crystallization from 1:1 methylene chloride–*n*-pentane afforded white plates (2.73 g, 70%) of **8**; mp 26–27 °C.

***O*-Phenyl-*N*,*N*-ditosylhydroxylamine (9).** Sodium hydride (912 mg, 50% in oil) was washed with *n*-hexane and suspended in 50 mL of freshly distilled THF with vigorous stirring at 0 °C, and after 30 min, *p*-toluenesulfonyl chloride (1.80 g) was added all at once. The whole was stirred for 3 h at room temperature, then diluted with water, and extracted with methylene chloride. The organic layer was dried over sodium sulfate and concentrated under reduced pressure at room temperature. The residual semisolid was crystallized from benzene–methylene chloride to give **9** (1.27 g, 64%): colorless needles; mp 117–118 °C. Anal. ($C_{20}H_{19}NO_5S$): C, H, N.

Acid-Catalyzed Reaction of 9 with Benzene. The procedure was the same as that for the reaction of **3** with benzene: **9** (417 mg, 1 mmol), 4.4 mL (50 mmol) of benzene, and 3.8 mL (50 mmol) of trifluoroacetic acid. After workup, the crude product was chromatographed, and the following compounds were isolated. (a) **4**: 34 mg (20%). (b) **5**: 8.5 mg (8%). (c) 2-Hydroxyphenyl *N*-ditosyl-*p*-toluenesulfonimidate (**10**): 133 mg (32%); colorless plates (from methylene chloride–*n*-hexane), mp 122–124 °C. Anal. ($C_{20}H_{19}NO_5S_2$): C, H, N. When the procedure described above was carried out in the absence of benzene, the yield of rearranged product **10** was 61%.

Hydrolysis of 10 to 7. A solution of 83.4 mg (0.2 mmol) of **10** in 5 mL of 2 N aqueous potassium hydroxide was heated under reflux for 30 min. The solution was acidified with concentrated hydrochloric acid and then extracted with methylene chloride. After evaporation of the solvent, the residual crystalline mass was recrystallized from methylene chloride–*n*-hexane to give **7** (45 mg, 85%), which was shown to be identical with an authentic sample by comparison of their IR spectra.

Acid-Catalyzed Reaction of 11 with Benzene. TFSA (2.65 mL, 30 mmol) was added to a solution of **11** (213 mg, 1 mmol) in 8.8 mL (100 mmol) of benzene with stirring. After 1 h, the stirred solution was diluted with water. The solution was neutralized with aqueous sodium hydrogen carbonate and then extracted with methylene chloride. After evaporation of the solvent, the crude product was chromatographed to give **4**, **5**, and catechol monobenzoate (**12**). The identification of **12** and an application of the rearrangement reaction from **11** to **12** were described in the previous paper.[14]

Acid-Catalyzed Reaction of 13 with Benzene. A solution of 277 mg (1 mmol) of **13** in 8.8 mL (100 mmol) of benzene was treated with trifluoroacetic acid (3.8 mL, 50 mmol) at 5 °C. After 1 h, the solution was worked up in a manner similar to that described for the reaction of **3** with benzene, and 47.8 mg (26%) of 2-hydroxy-5-methylbiphenyl (**14**) was isolated: colorless needles; mp 68–69 °C. Anal. ($C_{13}H_{12}O$): C, H. A 277-mg (1 mmol) sample of **13** was treated with 8.8 mL (100 mmol) of benzene, 3.8 mL (50 mmol) of trifluoroacetic acid, and 0.09 mL (1 mmol) of TFSA at 5 °C, and the following products were isolated. (a) **14**: 81 mg (44%). (b) 2,2′-dihydroxy-5,5′-dimethyl-*m*-terphenyl (**15**): 13 mg (9%); colorless needles; mp 185–186 °C. Anal. ($C_{20}H_{18}O_2$): C, H.

Acid-Catalyzed Reaction of 16 with Benzene. A solution of 308 mg (1 mmol) of **16** in 8.8 mL (100 mmol) of benzene was mixed with 3.8 mL (50 mmol) of trifluoroacetic acid and 0.88 mL (10 mmol) of TFSA, and the whole was stirred for 20 h at room temperature. After workup, the crude product was purified by chromatography to give 2-hydroxy-5-nitrobiphenyl (**17**): pale yellow needles; mp 124–125 °C. Anal. ($C_{12}H_9NO_3$): C, H, N.

Acid-Catalyzed Reaction of 3 with Anisole. TFA (3.8 mL, 50 mmol) and TFSA (0.09 mL, 1 mmol) were added to a solution of **3** (263 mg, 1 mmol) in 5.40 g (50 mmol) of anisole with stirring at 0 °C. After 1 h, the reaction mixture was diluted with water. The dilution was neutralized with aqueous sodium hydrogen carbonate followed by extraction with methylene chloride. The extract was dried over sodium sulfate and filtered. The solvent was evaporated off under reduced pressure at 50–60 °C. The crude product was chromatographed, and the following compounds were isolated. (a) 2-Methoxy-2′-hydroxybiphenyl: colorless needless; mp 71–72 °C (lit.[21] mp 71.5–73 °C). Anal. ($C_{13}H_{12}O_2$): C, H. (b) 4-Methoxy-2′-hydroxybiphenyl: colorless needles; mp 64–65.5 °C (lit.[22] 65–65.5 °C). Anal. ($C_{13}H_{12}O_2$): C, H. (c) A mixture of 2- and 4-methoxy-4′-hydroxybiphenyl; the products were isolated by fractional recrystallization from hexane. 2-Methoxy-4′-hydroxybiphenyl: colorless needles; mp 114–115 °C (lit.[23] 113–114 °C). Anal. ($C_{13}H_{12}O_2$): C, H. 4-Methoxy-4′-hydroxybiphenyl: colorless leaflets; mp 181–183 °C (lit.[24] mp 183–184 °C). Anal. ($C_{13}H_{12}O_2$): C, H. Gas chromatographic yields of 2- and 4-methoxy-2′-hydroxybiphenyl and 2- and 4-methoxy-4′-hydroxybiphenyl were 14.6%, 17.8%, 14.8%, and 17.5%, respectively.

Acid-Catalyzed Reaction of 3 with Phenol. TFA (3.8 mL, 50 mmol) and TFSA (0.09 mL, 1 mmol) were added to a solution of **3** (263 mg, 1 mmol) in 4.70 g (50 mmol) of phenol with stirring at 0 °C. After 1 h, the reaction mixture was worked up in a manner similar to that described for the reaction of **3** with anisole. The crude product was chromatographed on silica gel with 4:1 methylene chloride–ethyl acetate as the eluent, and the following compounds were isolated. (a) 2,2′-Dihydroxybiphenyl: colorless needles; mp 109–110 °C. Anal. ($C_{12}H_{10}O_2$): C, H. (b) 2,4′-Dihydroxybiphenyl: colorless needles; mp 159–161 °C. Anal. ($C_{12}H_{10}O_2$): C, H. (c) 4,4′-Dihydroxybiphenyl: colorless leaflets; mp 276–277 °C. Anal. ($C_{12}H_{10}O_2$): C, H. Gas chromatographic yields of 2,2′-, 2,4′-, and 4,4′-dihydroxybiphenyl were 9.2%, 32.7%, and 27.6%, respectively.

Acid-Catalyzed Reaction of 3 with Acetic Acid. A solution of 263 mg (1 mmol) of **3** in 4.3 mL (75 mmol) of acetic acid was treated with 0.53

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mL (6 mmol) of TFSA at room temperature. After 18 h, acetic acid was evaporated off under reduced pressure at 30 °C. The residue was diluted with water followed by neutralization with aqueous sodium hydrogen carbonate. The solution was extracted with methylene chloride. The extract was dried and concentrated. The resulting residue was chromatographed on silica gel with 5:1 methylene chloride–ethyl acetate to give **6** (39 mg; 16%), **7** (60 mg, 23%), and 4-acetoxyphenol (17 mg, 11%).

Acid-Catalyzed Reaction of 3 with 2,2,2-Trifluoroethanol. The procedure was the same as that for the reaction of **3** with acetic acid: 263 mg of **3**, 10 mL of trifluoroethanol, and 0.44 mL of TFSA. After workup, the product was separated by silica gel chromatography using 1:1 methylene chloride–*n*-hexane as the eluent to give **6** (19 mg, 8%), **7** (43 mg, 16%), 2-((trifluoro)ethoxy)phenol (6 mg, 3%) [mass spectrum, *m/e* 192 (M^+); ^1H NMR ($CDCl_3$) 4.36 (2 H, q, J = 8 Hz), 5.96 (1 H, s), 6.88 (4 H, s)], and 4-((trifluoro)ethoxy)phenol (61 mg, 32%) [mass spectrum, *m/e* 192 (M^+); ^1H NMR ($CDCl_3$) 4.39 (2 H, q, J = 8 Hz), 5.86 (1 H, s), 6.85 (4 H, s)]. The structure of ((trifluoro)ethoxy)phenol was deduced by acetylation to 4-((trifluoro)ethoxy)phenyl acetate: NMR ($CDCl_3$) 2.26 (3 H, s), 4.29 (2 H, q, J = 8 Hz), 6.85 (2 H, d, J = 9 Hz), 7.03 (2 H, d, J = 9 Hz). A similar reaction was carried out using BF_3 etherate (5 equiv) in 15 mL of trifluoroethanol. Gas chromatographic yields of 2- and 4-((trifluoro)ethoxy)phenol were 4.0% and 33.6%, respectively.

Acid-Catalyzed Reaction of 3 with Methanol. A solution of 263 mg of **3** in 4 mL of methanol was bubbled through with anhydrous BF_3 gas for 1 h at 0 °C. The solution was then poured into saturated aqueous sodium hdyrogen carbonate and extracted with methylene chloride. After evaporation of the solvent, the product was chromatographed to give **7** (55 mg, 21%), 2-methoxyphenol (4 mg, 3.2%), and 4-methoxyphenol (19 mg, 15%). Gas chromatographic yields of 2- and 4-methoxyphenol were 3.0% and 16.1%, respectively.

Acid-Catalyzed Reaction of 3 with Acetonitrile. The procedure was the same as that for the reaction of **3** with acetic acid: 263 mg of **3**, 5.25 mL of acetonitrile, and 0.2 mL of TFSA. After workup, the product was separated by silica gel chromatography using 3:2 methylene–EtOAc as the eluent to give 4-acetamidophenol (23 mg, 15%). In addition, an unidentified compound was obtained: 168 mg (55%); colorless plates; mp 176–177 °C; ^1H NMR ($CDCl_3$/Me_2SO-d_6) 2.40 (3 H, s), 2.46 (3 H, s), 6.5–7.8 (8 H, m), 8.95 (1 H, s), 9.70 (1 H, s). Anal. ($C_{15}H_{16}N_2O_3S$): C, H, N.

Acid-Catalyzed Reaction of 3 with Ethanethiol. A solution of 263 mg of **3** in 4 mL of methylene chloride and 7.47 mL of ethanethiol was bubbled through with anhydrous BF_3 gas for 1 h at 0 °C. After workup, the product was separated by silica gel column chromatography to give 2-ethylmercaptophenol (35 mg, 23%) and 4-ethylmercaptophenol (66 mg, 43%).

Acid-Catalyzed Reaction of 3 with Hydrogen Chloride. A solution of 263 mg of **3** in 2 mL of methylene chloride and 7.6 mL of trifluoroacetic acid was bubbled through with anhydrous hydrogen chloride for 2 h at room temperature. After workup, the product was chromatographed to give **7** (55 mg, 21%), 2-chlorophenol (22 mg, 17%), and 4-chlorophenol (13 mg, 10%). Gas chromatogrpahic yields of 2- and 4-chlorophenol were 18.0% and 13.5%, respectively.

Registry No. 1, 410711-17-4; **2**, 4846-21-3; **3**, 65109-75-3; **4**, 90-43-7; **5**, 92-69-3; **6**, 65109-80-0; **7**, 65109-81-1; **8**, 83076-97-5; **9**, 65109-77-5; **10**, 83076-98-6; **11**, 4380-77-2; **12**, 5876-92-6; **13**, 65109-76-4; **14**, 39579-09-4; **15**, 65109-83-3; **16**, 83076-99-7; **17**, 4291-29-6; *O*-(4-nitrophenyl)hydroxylamine, 33543-55-4; 4-nitrofluorobenzene, 350-46-9; ethyl acetohydroxamate, 10576-12-2; benzene, 71-43-2; anisole, 100-66-3; phenol, 108-95-2; 2-methoxy-2′-hydroxybiphenyl, 3594-88-5; 4-methoxy-2′-hydroxybiphenyl, 21849-91-2; 2-methoxy-4′-hydroxybiphenyl, 65109-82-2; 4-methoxy-4′-hydroxybiphenyl, 16881-71-3; 2,2′-dihydroxybiphenyl, 1806-29-7; 2,4′-dihydroxybiphenyl, 611-62-1; 4,4′-dihydroxybiphenyl, 92-88-6; ethyl *O*-(4-nitrophenyl)acetohydroxamate, 83077-00-3.

Experimental Evidence for the Intermediacy of Singlet (S_1) and Triplet (T_2) n,π* States in the [1,3]-Sigmatropic Acyl Shift of Photoexcited 3-Methyl-3-(1-cyclopentenyl)butan-2-one†[1]

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Abstract: A series of photochemical investigations of the title compound, a model β,γ-unsaturated ketone, has been carried out to differentiate between reaction pathways resulting in a [1,3]-sigmatropic acyl shift originating in singlet and triplet n,π* excited states, S_1 and T_2, respectively. These include studies of differential sensitization and quenching of photoreactions, dependence of quantum efficiencies for fluorescence and product formation on temperature, and, finally, the perturbation on these quantities induced by irradiation in the presence of xenon. The results suggest that the [1,3]-sigmatropic acyl shift can occur from both S_1 and T_2 excited states and that the reaction from S_1 requires thermal activation. Intersystem crossing from S_1 to T_2 is enhanced in the presence of xenon, the first example of such heavy-atom enhancement in ketone photochemistry. This particular radiationless transition is not in accord with predictions based on El-Sayed's rules. Furthermore, in this system, reaction from T_2, initiated by α cleavage, appears to occur to the exclusion of decay to T_1, which is the origin of the oxa-di-π-methane rearrangement pathway. The lowest triplet T_1 can only be populated by triplet energy transfer from appropriate sensitizers.

The photochemistry of β,γ-enones is quite rich due to the presence of nearby but unconjugated alkene and carbonyl chromophores.[2] In addition to reactions characteristic of the separate chromophores, there are two reactions of these enones that depend on bichromophoric interactions, namely, the [1,3]- and [1,2]-sigmatropic acyl shifts (1,3- and 1,2-SAS) illustrated in Scheme I. The latter reaction is also known as the oxa-di-π-methane (ODPM) rearrangement.

A large number of investigations[2] allow the conclusion that the ODPM rearrangement arises from the lowest π,π* triplet state

† Dedicated to George S. Hammond on the occassion of his 61st birthday, in recognition of his many important contributions to the science of organic photochemistry.

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