Singlet Quenching. Fluorescence quenching measurements were carried out by using a Spex fluorolog digital spectrofluorimeter. Sensitizers selected for study were those with significant absorption at wavelengths greater than 380 nm, so that competitive absorption by di-*tert*-butyl peroxide ($\epsilon_{380} = 0.031\ M^{-1}\ cm^{-1}$) was minimized. Quencher concentrations ranged from 0.1 to 1.5 M, and the resulting Stern-Volmer plots were acceptably linear. The solutions (in benzene) were not deaerated. Fluorescence lifetimes for fluorenone[50] and anthracene[51] in air-saturated benzene were available in the literature. The literature values for phenanthrene ($\tau_F = 57.4$ ns)[18] and benz[*a*]anthracene ($\tau_F = 26$ ns)[52] were corrected for oxygen quenching by the formula $\tau_{air} = 1/(\tau_F^{-1} + k_{O_2}[O_2])$. The values of $[O_2]$ and k_{O_2} were taken to be 1.91×10^{-3} M and $3.0 \times 10^{10}\ M^{-1}\ s^{-1}$, respectively.[53] This procedure and the use of literature lifetimes introduce the possibility of up to 25% error in our quenching rate constants.

Triplet Quenching. Our laser flash photolysis facility makes use of a Molectron UV-400 nitrogen laser for excitation. The pulses (8 ns, ~3 mJ, 337.1 nm) are concentrated on the sample and are incident at an angle of approximately 15°. The excitation doses were adjusted with suitable neutral density filters in order to avoid triplet-triplet annihilation processes. The system is fully interphased with a PDP 11/55 computer; further details on the instrument and technique have been given elsewhere.[54,55]

The concentration of sensitizers was chosen so as to obtain an optical density between 0.3 and 1.0 at 337.1 nm in a cell with an optical path of 3 mm.

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Acid-Catalyzed Reactions of *N*-Arylhydroxylamines and Related Compounds with Benzene. Iminium-Benzenium Ions

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Abstract: *N*-Arylhydroxylamines react with benzene in the presence of trifluoroacetic acid (TFA) at room temperature to give diphenylamines. When TFA was replaced by a strong acid, trifluoromethanesulfonic acid (TFSA), the major products were aminobiphenyls. The nature of the reaction was explored by reactions of 4-substituted phenylhydroxylamines and dialkylaniline *N*-oxides with benzene. Thus, it was demonstrated that the reactive intermediates are onium-benzenium dications which are trapped by benzene to give aminobiphenyls by a mechanism similar to the Friedel-Crafts alkylation. Further evidence for the proposed reaction mechanism was the observation that nitrosobenzene and azoxybenzene reacted with benzene to give analogous products in the presence of the stronger acid.

Introduction

Although *N*-arylhydroxylamines have been known since the last century,[1,2] their nature and reactivity are still not sufficiently understood.[3] The chemistry of *N*-arylhydroxylamines is currently important in the study of the metabolism of nitrogen compounds.[4] Particularly, interesting are the metabolically activated forms of many nitro and amino carcinogens, which are often *N*-arylhydroxylamine derivatives.[5,6] Some activated carcinogens have been shown to react with bionucleophiles via attack at the nitrogen atom or the carbon atom of an intermediate *N*-arylhydroxylamine.[6-8]

Acid-catalyzed "rearrangement" of *N*-phenylhydroxylamine to 4-aminophenol in sulfuric acid was reported by Bamberger.[1,9,10] His excellent work and later studies by others[11-14] have shown that the reaction is intermolecular with water (or sulfate) and other groups such as halogen and alkoxyl as the attacking nucleophile. Bamberger also reported that *N*-phenylhydroxylamine reacts with aniline, phenol, and 4-nitrotoluene.[10]

In 1920, Kliegl and Huber reported that aminobiphenyl and diphenylamine are formed in the $AlCl_3$-catalyzed reaction of *N*-(4-methylphenyl)hydroxylamine with benzene.[15] More recently Whiting reported a similar reaction catalyzed by tetrafluoroboric acid in sulfolane.[16]

We have explored further the reactivity of *N*-arylhydroxylamines, attempted to rationalize and generalize their reactions, and to clarify the mechanism involved.[17] In this paper regiose-

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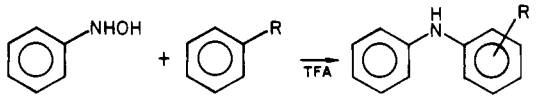
lective reactions of *N*-arylhydroxylamines are reported and the mechanisms discussed.

Diphenylamine Synthesis

Our interest in the chemistry of *N*-arylhydroxylamines was initiated by a study of the trifluoroacetic acid (TFA)-catalyzed reaction of *N*-arylhydroxylamine with benzenes.[17a] TFA was chosen because of its low nucleophilicity, thereby reducing competition with weak nucleophiles such as benzene.

N-Arylhydroxylamine was added to a mixture of TFA and an aromatic compound at 0–5 °C or at room temperature under a nitrogen atmosphere. The fundamental reaction of *N*-phenylhydroxylamine (**1**) with benzene gave diphenylamine (**2**) in 66% yield (eq 1). The reproducibility was improved by the presence



(1)

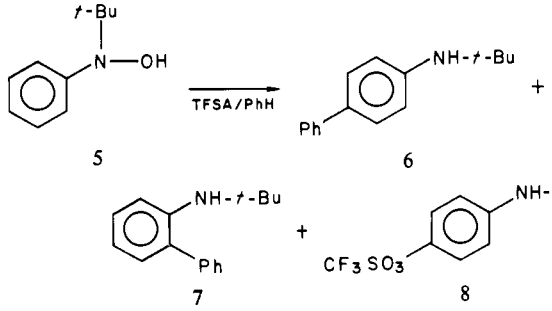
1

2, R = H
3a, R = 4-CH_3, **3b**, R = 2-CH_3
4a, R = 4-OCH_3, **4b**, R = 2-OCH_3

of a radical scavenger, L-ascorbic acid. Reaction of **1** with toluene in the presence of ascorbic acid gave 4-methyldiphenylamine (**3a**) and 2-methyldiphenylamine (**3b**) in 56 and 21% yields, respectively. Reaction of **1** with anisole proceeded similarly to give 4-methoxydiphenylamine (**4a**) and 2-methoxydiphenylamine (**4b**) in 26 and 14% yields, respectively. Similarly *N*-(4-methylphenyl)hydroxylamine reacted with anisole to give 4-methoxy-4′-methyldiphenylamine in 66% yield.

Aminobiphenyl Synthesis

The TFA-catalyzed reaction of **1** gave a small amount of aminobiphenyl in addition to **2**. Therefore we sought to modify the reaction to favor this alternative pathway.[17b] For this purpose, *N-tert*-butyl-*N*-phenylhydroxylamine (**5**)[18] was chosen, because the steric bulk of the *N-tert*-butyl group should hinder attack at the nitrogen atom. However, the TFA-catalyzed reaction of **5** with benzene was very slow, even at reflux when a complex mixture of products was formed. Among the products identified were **2** (12%), 4-aminobiphenyl (6%), 2-aminobiphenyl (2%), 4-(*N-tert*-butylamino)biphenyl (5%), 2-(*N-tert*-butylamino)biphenyl (1%), and azoxybenzene (5%), and 30% of **5** was recovered. *N-tert*-Butyldiphenylamine was not isolated. A large recovery of starting material indicated that this reaction was significantly suppressed by ascorbic acid. When trifluoromethanesulfonic acid (TFSA), a stronger acid than TFA, was substituted for TFA in the reaction of **5** with benzene, the desired product was smoothly formed by attack on the benzene ring giving (*N-tert*-butylamino)biphenyls, **6** and **7**, in yields of 49% and 8%, respectively, together with a sulfonyl ester (**8**, 10%) (eq 2).



(2)

5 6 7 8

This result led us to reexamine the reaction of **1** with benzene in the presence of TFSA. The dramatic effect of TFSA is shown in Table I. In the presence of TFA, the major product was **2**. The addition of TFSA changed the reaction site. In the presence

(17) (a) Shudo, K.; Okamoto, T. *Tetrahedron Lett.* **1973**, 1839. (b) Okamoto, T.; Shudo, K.; Ohta, T. *J. Am. Chem. Soc.* **1975**, *97*, 7184. (c) Ohta, T.; Shudo, K.; Okamoto, T. *Tetrahedron Lett.* **1976**, 101. (d) Shudo, K.; Ohta, T.; Endo, Y.; Okamoto, T. *Ibid.* **1976**, 105.

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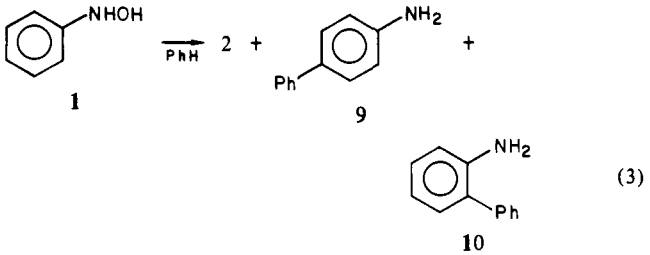
Table I. Reaction of *N*-Phenylhydroxylamine (**1**) with Benzene

run	amounts of acids,[a] mol CF_3CO_2H	amounts of acids,[a] mol CF_3SO_3H	benzene,[a] mol	procedure	products,[b] % 2	9	10
1	4	0	3.5	*c, e, g*	41	3	3
2	10	0	9.0	*c, e, g*	56	9	8
3	25	0	22.0	*c, e, g*	46	12	11
4	25	0	22.0	*c, e*	12	5	5[h]
5	25	0.2	22.5	*c, e*	20	4	4
6	25	1.2	22.5	*c, f*	39	19	17
7	25	2.3	22.5	*c, f*	14	46	25
8	0	2.0	60.0	*d, f*	2	25	12
9	0	4.0	60.0	*d, f*	1	32	16
10	0	20.0	60.0	*d, f*	1	48	23

[a] Moles per mole of **1**. [b] Based on VPC. [c] **1** was added to a stirred mixture of acid(s) and benzene at 5 °C. [d] TFSA was added dropwise to a mixture of 1 and benzene at 5 °C. [e] For 12 h. [f] For 30 min. [g] In the presence of catalytic amount of ascorbic acid. [h] Azoxybenzene was the major product.

of more than 4 equiv of TFSA, reaction at the nitrogen was suppressed, and only 4-aminobiphenyl (**9**, 48%) and 2-aminobiphenyl (**10**, 23%) were obtained (see eq 3). The presence or

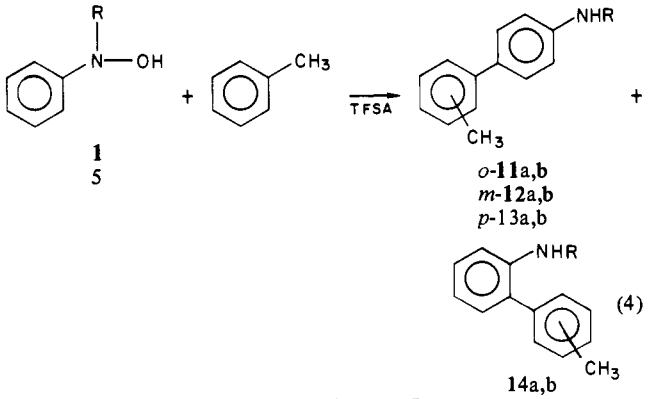


(3)

1 9 10

absence of TFSA, and not the polarity of the medium, appeared to be the controlling factor (compare runs 3 and 7 in Table I). The reaction was very rapid and proceeded below 5 °C. Light and air did not alter the reaction products and rate. No azoxybenzene or biphenyl, indicative of a homolytic pathway, were detected in the TFSA-catalyzed reaction. Both diphenylamine and aminobiphenyls was stable under the reaction conditions. The ortho and para positions of **1** were phenylated in synthetically useful yields.

Reaction of **1** with toluene in the presence of TFSA gave a mixture of aminomethylbiphenyls (eq 4). 4-Aminomethylbi-



(4)

1 5

o-**11a,b**
m-**12a,b**
p-13a,b

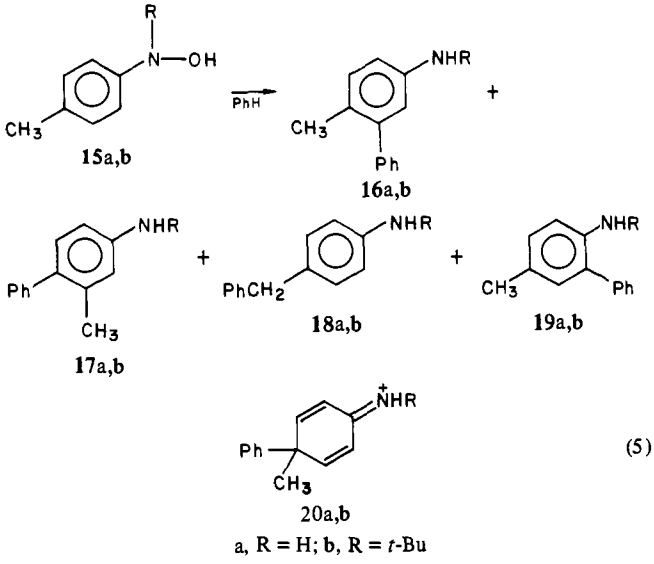
14a,b

a, R = H; b, R = *t*-Bu

phenyls (**11a**, **12a**, and **13a**) were separated by VPC, and the structures of **12a** and **13a** were verified by independent syntheses, and their UV spectra were very similar to related compounds (see Experimental Section). The product ratio was determined by NMR; the mixture of 4-aminomethylbiphenyl (40% yield) consisted of 45% ortho, 22% meta, and 32% para isomers. This result suggests that significant reaction occurred at the meta position of toluene. The isomer ratio of 2-aminomethylbiphenyls (**14a**, 23% yield) was not determined. A similar result was obtained in the reaction with **5**; the ortho:meta:para ratio of 4-(*N-tert*-

butylamino)methylbiphenyls (46% yield) was 39:24:37. In this case, the yield of 2-(*N-tert*-butylamino)methylbiphenyls (**14b**) was only 7%, reflecting the steric bulk of *tert*-butyl group. The estimated errors associated with the product distributions reported were about ±2%.

Reaction of *N*-(4-methylphenyl)hydroxylamine (**15a**) and *N-tert*-butyl-*N*-(4-methylphenyl)hydroxylamine (**15b**) with benzene in TFSA–TFA gave an interesting result. One of the major products was **16a** (24%) which may formally be regarded as being produced by meta substitution. The presence of **17a** in the reaction, although in low yield, suggests that **16a** and **17a** are formed by rearrangement of an intermediate cyclohexadienimininium ion (**20a**), the phenyl group being the better migrating group. Compound **17a** was the major product in the reaction of *N*-(3-methylphenyl)hydroxylamine with benzene, giving further evidence for the structure of **17a**. The UV spectra were also consistent with the proposed structures. The minor product, **18a** (7%), was formed by attack of benzene at methyl group, and its structure was confirmed by an independent synthesis. The ortho-substituted product (**19a**, 37%) was also obtained. Reaction of *N-tert*-butyl-*N*-(4-methylphenyl)hydroxylamine (**15b**) with benzene gave a similar result: **16b** (44%), **17b** (3%), **18b** (17%), and **19b** (18%) (see eq 5).



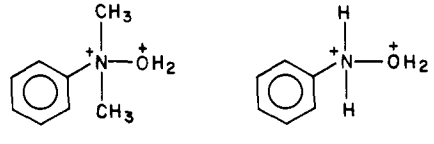
(5)

a, R = H; b, R = *t*-Bu

Substituted *N*-phenylhydroxylamine with nucleofugal leaving groups such as methoxyl and chloro at the para position of the phenyl group reacted with benzene under similar conditions to give terphenylamines (**21** and **22**) and **9** which lost the nucleofugal groups. These products were also obtained by the reaction of *N*-(4-biphenyl)hydroxylamine (**24**) with benzene; the yields and the structures are shown in Scheme I. Terphenylamines (**21** and **22**) were identified by comparison with authentic samples. In the ortho-phenylated products (**23**) the methoxyl and chloro groups were retained. Although aniline was not formed in the TFSA-catalyzed reaction of **1** with benzene, the reaction with **24** gave a considerable amount of **9**.

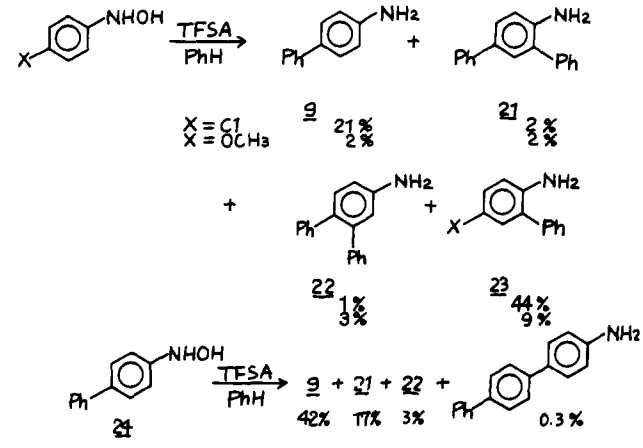
N,*N*-Dimethylaniline *N*-Oxide

To provide further information about the mechanism and synthetic pathways, we studied the related acid-catalyzed reaction of *N*,*N*-dimethylaniline *N*-oxide (**25**) with benzene.[17d] A diprotonated *N*-oxide is isoelectronic with N,O-diprotonated *N*-phenylhydroxylamine.

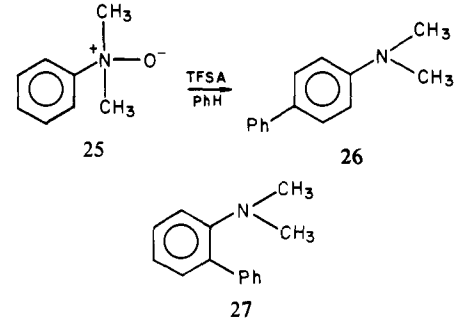


A mixture of **25**, benzene (60 equiv) and TFSA (10 equiv) was stirred for 24 h at room temperature (see eq 6). The products

Scheme I

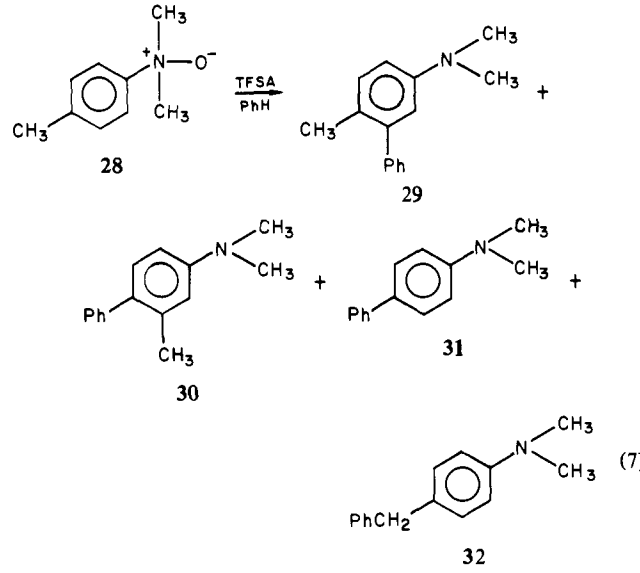


isolated were 4-(*N*,*N*-dimethylamino)biphenyl (**26**, 64–76%) and 2-(*N*,*N*-dimethylamino)biphenyl (**27**, 4–6%). No reaction occurred when TFA was substituted for TFSA.



(6)

The TFSA-catalyzed reaction of *N*,*N*-dimethyl-4-toluidine *N*-oxide (**28**) with benzene (eq 7) is very similar reaction to that



(7)

of **15a** and **15b**. The major product was 5-(*N*,*N*-dimethylamino)-2-methylbiphenyl (**29**, 46%). Isomeric products **30** (2%), **31** (8%), and **32** (4%) were also isolated. This product composition is very similar to that obtained by reaction of **15a** and **15b** with benzene. This suggests strongly that the same kind of intermediate participates in both reactions.

In addition to acid catalysis, the reaction of **25** with benzene was also effected by trifluoroacetic anhydride at room temperature in the presence or absence of sodium bicarbonate. Although the major product was an acetoxy migration product,[19] **26** was isolated

(19) Huisgen, R.; Bayerlein, F.; Heykamp, W. *Chem. Ber.* **1959**, *92*, 3223.

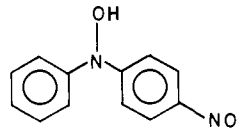
in 1–2% yield. In the presence of 2–4 equiv of TFA and trifluoroacetic anhydride, the yield of **26** increased to 7%. In the presence of TFA alone, **25** did not react with benzene. Acetic anhydride was not effective.

Nitroso-, Azo- and Azoxybenzenes

It has been claimed that the *N*-hydroxy- or *N*-anilinoanilenium ion is involved in the bromination of nitrosobenzene and azobenzene. We have investigated the phenylation of nitroso-, azo-, and azoxybenzenes.[17c] Examples of analogous phenylation reactions can be found in the work of Bandrowski,[20] Kliegl,[15] and Pummerer,[21] but these early reports have generally aroused little interest.

Reaction of nitrosobenzene (**33**) with benzene (60 equiv) in the presence of TFSA (10 equiv) and TFA (20 equiv) proceeded very rapidly at 0–5 °C (eq 8). The products were **21** (27%), **22** (3%),

33



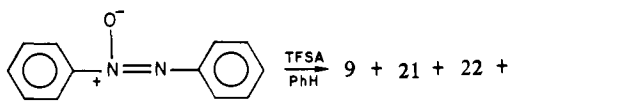
34 (8)

and **9** (31%). In the presence of 30 equiv of TFSA, **9** (47%), **10** (9%), **21** (4%), **22** (1%), and **2** (2%) were the products. On the other hand, reaction of **33** in the presence of TFA alone obtained (4-nitrosodiphenyl)hydroxylamine (**34**) as reported earlier.[22] The formation of **21**, **22**, **9**, and **10** required the stronger acid, TFSA. These products **21**, **22**, and **9** were also obtained by the reaction of **24** with benzene under similar conditions.

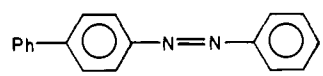
Azobenzene (**35**), a compound isoelectronic with nitrosobenzene, reacted similarly with benzene in the presence of TFSA (see eq 9). The reaction was much slower than that of nitrosobenzene, and a higher temperature (80 °C, 24 h) was required; the products were **9** (77%), **21** (3%), and **22** (1%). The overall result is similar to the reaction of **33**.

35 (9)

Examination of azoxybenzene (**36**) as a substrate was of particular interest because of the direct analogy with the Wallach rearrangement.[23,24] Reaction of **36** with benzene in the presence of TFSA or TFSA–TFA proceeded smoothly at 40 °C (see eq 10). The major product was **9** (74%). Aminoterphenyls **21** (4%)



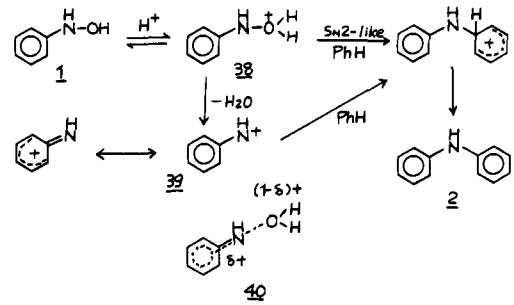
36



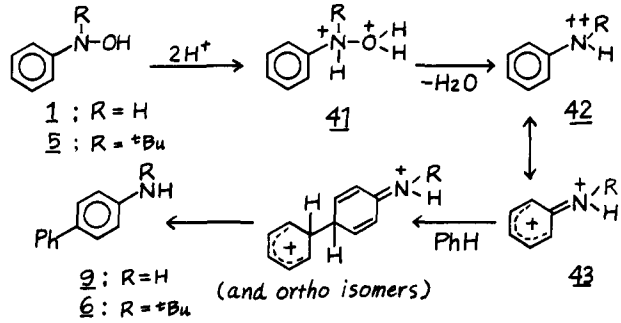
37 (10)

and **22** (1%) were also obtained, and 4-phenylazobenzene (**37**) was isolated in 0.5% yield (catalyzed by TFSA–TFA but not TFSA alone). It was interesting that the addition of base (2–4 equiv of potassium salt of TFSA or tertiary amines) increased the yield of **37** up to 20%, probably via catalysis of the hydrogen shift or proton abstraction from the intermediate. Since **37** was stable under the reaction conditions, **37** was not the intermediate which led to **21**, **22**, and **9**.

Scheme II



Scheme III



Mechanism

The TFA-catalyzed reaction of *N*-arylhydroxylamine with benzene gave diphenylamine, while TFSA (or TFSA–TFA)-catalyzed reaction of *N*-arylhydroxylamine gave aminobiphenyls (Table I).

Diphenylamine was formed by attack of benzene with elimination of a water molecule. The reaction was smoother in the presence of a radical scavenger which suppresses the formation of azoxybenzene by a homolytic pathway. The ortho/para orientation and more facile reaction with *N*-arylhydroxylamine bearing electron-donating substituents are consistent with an ionic reaction involving an electrophilic species derived from *N*-arylhydroxylamine. It seems natural to assume that the reaction involves an O-protonated *N*-phenylhydroxylamine (**38**) which may be in equilibrium with other protonated species, followed by a heterolytic cleavage of the N–O bond (Scheme II). This is similar to the proposed mechanism of the acid-catalyzed rearrangement of *N*-phenylhydroxylamine, the Bamberger rearrangement.[2,11,25] The good positional selectivity of the reaction suggested that the attacking species is not very reactive. From this and the slower reaction of *N*-*tert*-butyl-*N*-phenylhydroxylamine, a bimolecular, acid-catalyzed S_N2-like substitution (A2)[26] at the nitrogen atom seems to be the most plausible mechanism (path a) although a mechanism which involves a free or almost free anilenium ion (**39**)[27] (path b) cannot be completely ruled out. We prefer a mechanism which involves a polarized O-protonated *N*-phenylhydroxylamine (**40**) with some anilenium ion character as the electrophilic species attacking the benzene molecule, essentially an A2 mechanism.

Any mechanism for the formation of aminobiphenyls must explain the role of the strong acid. The acidity of TFSA (H_0 = −14)[28] is so high that diprotonation of **1** is very likely. A possible

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(21) Pummerer, R.; Binapfl, J. *Ber. Dtsch. Chem. Ges.* **1921**, *54*, 2768.
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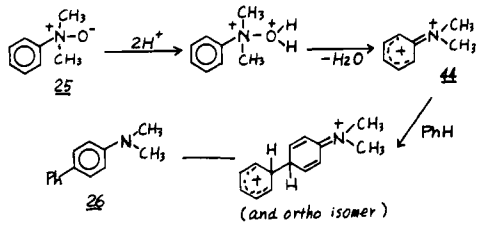
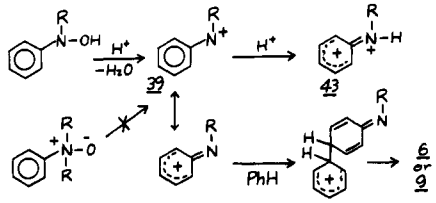
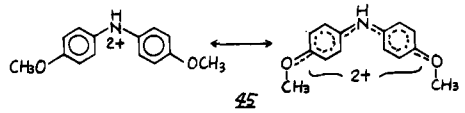
Scheme IV



Scheme V



mechanism involves a protonated anilenium ion (**42**) which may be formed from N,O-diprotonated *N*-phenylhydroxylamine (**41**) (Scheme III). Since the charge of the dication (**42**) is undoubtedly delocalized over the aromatic ring, the species has to be regarded as an iminium–benzenium dication (**43**) rather than a protonated anilenium ion. This doubly charged ion must be very reactive toward benzene in a similar way to the Friedel–Crafts reaction. The high reactivity of this intermediate was reflected in a rapid reaction of 0 °C and the low regioselectivity in the reaction of **1** with toluene. It is known that the regioselectivity is lost when the reactivity of an electrophile is high.[29] A similar scheme for the reaction of *N*-oxide (**25**) with benzene, where the intermediate is an *N,N*-dimethyliminium–benzenium ion (**44**), is shown in Scheme IV. This ion reacts with benzene in a similar way to the above. A closely related species, the protonated dianisylnitrenium ion (**45**), has been reported.[30] This dication is stabilized



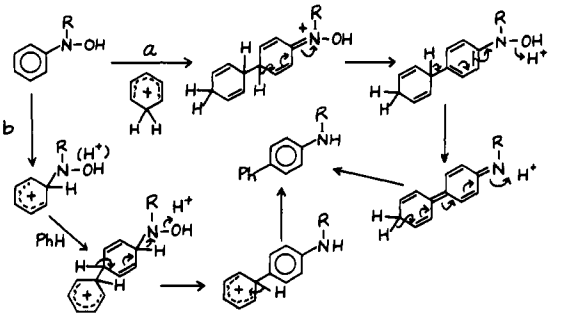
by two methoxy-substituted aromatic rings and can be isolated as a stable species. The intermediates (**43** and **44**) have only one aromatic ring, and the positive charge is necessarily located on the single benzenium moiety. Therefore, these intermediates are quite reactive toward benzene.

The protonated anilenium ion (**43**) may also be formed by protonation of the anilenium ion (**39**) which arises from S_N1-type reaction of monoprotonated *N*-phenylhydroxylamine (**38**) or *O*-(trifluoromethanesulfonyl)-*N*-phenylhydroxylamine (Scheme V). However, this seems unlikely from the result of *N*-oxide (**25**), which can never yield an anilenium ion.

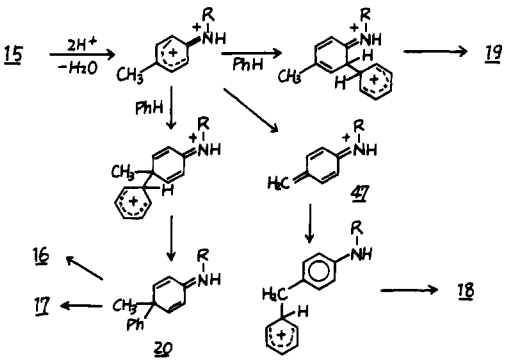
A simpler explanation would be the participation of anilenium ion (**39**) itself, which leads to phenylated products by some reasonable electron-pair shifts. This explains many of the products and does not require the postulation of a reactive intermediate such as the doubly charged ion. However, this mechanism neglects the most important role of the acid; the regioselectivity of the reaction is completely controlled by acidity. The analogous reaction of **25** which cannot give an anilenium ion rules out this mechanism.

A Scholl-type reaction,[31] which involves a protonated benzene, benzenium ion, is another possibility (Scheme VIa). Protonation

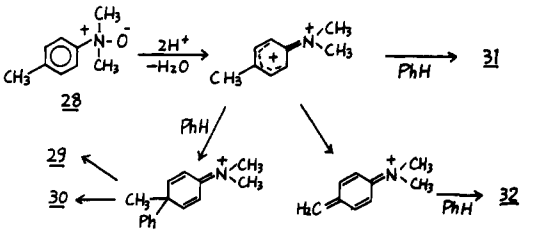
Scheme VI



Scheme VII



Scheme VIII



at the ipso position of the hydroxylamino group also is possible;[32] the benzenium ion might attack the benzene molecule (Scheme VIb). However, these mechanisms do not account for the formation of **18** and **32** from **15** and **28**, respectively. Reaction of **25** with benzene by acylation with trifluoroacetic anhydride also rules out a Scholl-type mechanism. The reaction catalyzed by trifluoroacetic anhydride is easily explained by the elimination of the trifluoroacetoxy group.

The products in the reaction of **15** are reasonably explained by the mechanism shown in Scheme VII. The major product is formally formed from attack at the meta position of **15** by benzene. It is plausible that primary attack is at the ipso position because rearrangement of the methyl group to the meta position can be reasonably understood by an intermediate cyclohexadieniminium ion (**20**), whereby the rearrangement of the phenyl group predominantes. The formation of the diphenylmethane derivative is considered as the reaction of a triene (**47**) with benzene. Thus, the complete sequence of the reaction of **15a,b** may be as shown in Scheme VII.

Exactly the same mechanism for the reaction of **28** as shown in Scheme VIII might be justified. A similar rearrangement was observed in the reaction of **24** with benzene (see eq 11). One of the major products was **22** whose formation suggests the 4,4-diphenyl derivative (**49**) as an intermediate.

Ipso attack, while leads to elimination instead of rearrangement, was observed in the reaction of *N*-(para-substituted phenyl)-hydroxylamine with a nucleofugal leaving group (Scheme IX). The products from these *N*-arylhydroxylamines included the re-

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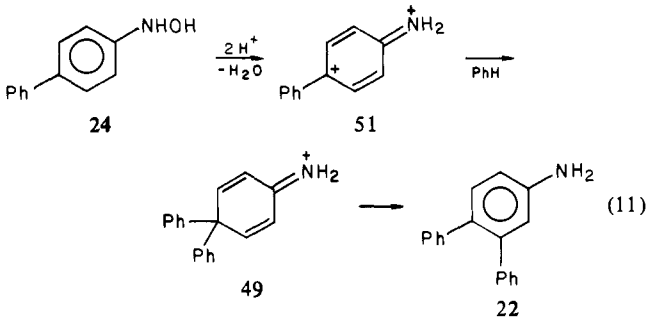
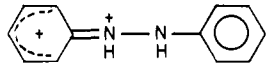


action products (**9**, **21**, and **22**) of **24** in addition to 2-aminobiphenyls with a 4-chloro or 4-methoxyl substituent. The ipso attack mentioned above gives a 4,4-disubstituted intermediate (**50**). The nucleofugal character of Cl and OCH_3 caused elimination to give the same cationic species (**51**) as formed in the acid-catalyzed reaction of **24**. This cation then reacts with benzene to give the 4,4-diphenyl intermediate (**49**) which rearranges to **22**. One unsolved problem is the reductive formation of **9** in these reactions; **1** and **15** did not yield the reduced amines.

The TFSA-catalyzed reaction of nitrosobenzene (**33**) gave a similar mixture of products to the reaction of **24** with benzene. The formation of biphenylamine and terphenylamine required an acid with high acidity, while TFA-catalyzed reaction followed a different pathway. The most plausible mechanism in the high acidity medium involves a diprotonated nitrosobenzene (**52**), i.e., an *N*-hydroxyiminium–benzenium ion (Scheme X). This ion reacts with benzene in a manner similar to that of **43**. By deprotonation the first formed intermediate gives **24** which then reacts with another benzene giving aminobiphenyls (**9** and **10**) and terphenylamines (**21** and **22**). Recently, Olah has observed diprotonated 4-hydroxynitrosobenzene (**53**) as a stable species and proposed similar species with a 4-hydroxy group as an electron donor.[33] The transient but distinct existence of the diprotonated nitrosobenzene (**52**) is most plausible, since there is no bond breakage in the formation of this species. **52** has no stabilizing group and, therefore, is so reactive that benzene is attacked. Since a reasonable analogy exists between this reaction and the reaction of **1** and **25**, the rate-determining formation of the iminium–benzenium ion is likely in all the cases.

Reaction of azobenzene is readily interpreted by the diprotonated species (**54**). However, the reaction was much more slower than the reaction of nitrosobenzene.



54

Azoxybenzene (**36**) reacted with benzene. In a strongly acidic medium, **36** yields a stable dicationic species (**55**),[24,34] a kind of delocalized iminium–benzenium dication. There is ample evidence for the existence of this dication.[24] It should be more stable than the iminium–benzenium ions (**43** and **44**) since the charge is delocalized over two aromatic rings (Scheme XI). The reaction of the cation (**55**) proceeded with the attack of benzene, although it required a high temperature (40 °C). From the first formed intermediate **56**, further reactions similar to nitrosobenzene occurred and the isolated products were terphenylamines and biphenylamines. However, in the presence of a conjugate base (the presence of added tertiary amines, trifluoromethanesulfonate, or trifluoroacetic acid, although the last was less effective), 4-phenylazobenzene (**37**) was obtained as one of the major products. Since this azobenzene was stable under the reaction conditions, it is not the intermediate to the biphenylamines or terphenylamines. Probably the role of the base is to catalyze deprotonation or proton migration from the intermediate; i.e., **56** to **37**. **56** further reacts with benzene to give terphenylamines by a multistep process. The

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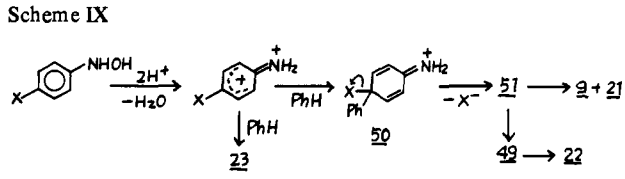
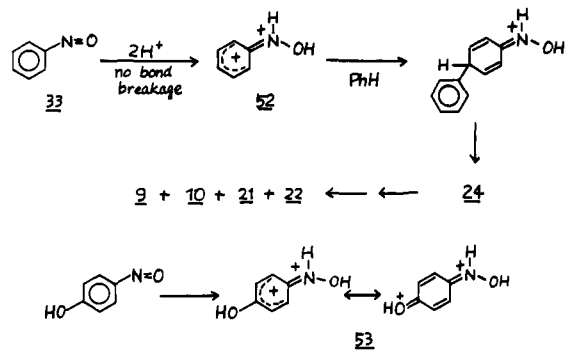
(34) Olah, G. A.; Dunne, K.; Kelly, D. P.; Mo, Y. K. *J. Am. Chem. Soc.* **1972**, *94*, 7438.

Scheme IX



Scheme X



Scheme XI

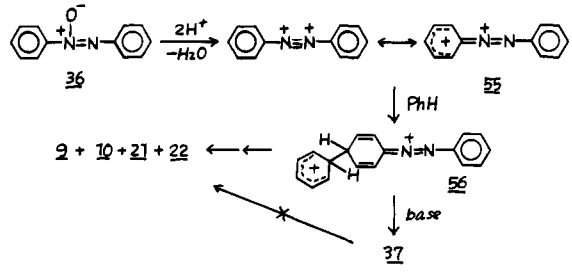
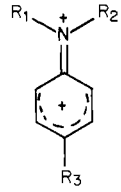


Table II. Iminium-Benzenium Ions



57

R_1	R_2	R_3	
H	H	H	43
t-Bu	H	H	43
CH_3	CH_3	H	44
4-OCH_3Ph	H	OCH_3	45
OH	H	H	52
OH	H	OH	53
NHPh	H	H	54
=N–Ph		H	55

reaction of azoxybenzene also supports the posturate of a doubly charged intermediate ion. The lower reactivity of azoxybenzene compared with **1** and **25** may be the result of the higher N–O bond energy of an azoxy group and the more highly stabilized intermediate.

Conclusion

A generalization of the acid-catalyzed reactions of *N*-arylhydroxylamine is summarized as follow. In TFA, the reaction center is the nitrogen atom and nucleophilic attack by benzene probably proceeds in an S_N2-like manner at the nitrogen atom of the O-protonated *N*-phenylhydroxylamine with some anilenium ion character (Scheme II). In TFSA or TFSA–TFA, a very reactive dicationic intermediate, the iminium–benzenium ion, takes part in the reaction (Scheme III). Participation of this species is supported by the similar reactions of *N*,*N*-dimethylaniline *N*-oxides and nitrosobenzene with benzene. Few such species have

been proposed before, and diprotonated nitrosophenol is an example of this kind of species. All such intermediates may be classified as iminium–benzenium ions with substituent(s) on the benzenium ring or the nitrogen atom (**57**) (Table II). These species are electrophilic and react with benzene by a Friedel–Crafts type mechanism when their reactivity is high enough.

The fundamental reaction is quite general, and the yield is good in the cases of *N*-arylhydroxylamines and *N,N*-dimethylaniline *N*-oxides. Synthetic applications in connecting two aromatic rings by this method look promising, and a few applications have already reported.[17d,35] This method has also been successfully applied to intramolecular coupling of two functionalized aromatic rings and the results are to be reported elsewhere.

Experimental Section

Melting points are uncorrected. NMR spectra were recorded ($CDCl_3$ with Me_4Si as internal standard) on a JEOL JNM-PS-100 spectrometer; all chemical shifts are reported in δ values. UV spectra were recorded in 95% ethanol as solvent unless otherwise mentioned on a Hitachi EPS-2U spectrometer.

TFA-Catalyzed Reaction of 1 with Benzene. To a cooled solution of benzene (2 mL) and TFA (2 mL) containing 10 mg of ascorbic acid was added **1** (200 mg) with sitrring. The mixture was allowed to react for 36 h at room temperature. After evaporation of benzene and TFA, aqueous K_2CO_3 was added and mixture was extracted with methylene chloride. Evaporation of the solvent gave 290 mg of a crude crystalline mass. Recrystallization from ethanol–water gave pure **2** (190 mg; 61%), mp 54–54.5 °C. Chromatographic separation of the mother liquor gave 4 mg of **9**, mp 52.5–53.5 °C. The yield determined by VPC was 60–72% for **2** and 4% for **9**.

TFA-Catalyzed Reaction of 1 with Toluene. The reaction was performed as above by using 2 mL of toluene. Silica gel column chromatography gave **3b** (oil, distilled at 150 °C (5mmHg)) in a yield of 17–20% and **3a** (mp 88–88.5 °C, 51–56%). These products were identified by comparison of IR spectra and mixture melting point with authentic methyldiphenylamines which were prepared by Ullmann condensation of *o*-, *m*-, or *p*-acetotoluidine and bromobenzene in the presence of potassium carbonate, copper powder, and iodine in nitrobenzene.

TFA-Catalyzed Reaction of 1 with Anisole. The crude reaction mixture obtained as above was purified by silica gel column chromatography. Compounds **4b** (oil, 120 °C (20mmHg), 14%) and **4a** (mp 108–108.5 °C, 26%) were obtained. In the reaction without ascorbic acid, the major product was azoxybenzene (5–40% yield), and the two methoxydiphenylamines were obtained in variable yields. Authentic methoxydiphenylamines were prepared by Ullmann reaction of *o*- or *p*-acetoanisidine and bromobenzene.

TFA-Catalyzed Reaction of 15a with Anisole. The TFA-catalyzed reaction of **15a** gave 4,4′-dimethylazobenzene (10.4%) and 4-methyl-4′-methoxydiphenylamine (mp 84–84.5 °C, 65.8%). Both compounds were identified by comparison of IR spectra and mixture melting point with authentic samples.

TFA-Catalyzed Reaction of 5 with Benzene. A mixture of 300 mg of **5**, 9 mL of TFA, and 9 mL of benzene was heated at 80 °C for 6 h. After workup 75 mg of the starting material was recovered by recrystallization of the crude reaction mixture from hexane. The products were analyzed by GC–MS and VPC (10% SE 30) using phenanthrene as the internal standard which showed 12% of **2**, 6% of **9**, 5% of **6**, 2% of **10**, 1% of **7**, and 5% of azoxybenzene. In the presence of ascorbic acid, most of the starting material was recovered.

TFSA-Catalyzed Reaction of 5 with Benzene. A 500-mg sample of **5** was added to 8 mL of TFA and 2 mL of TFSA, in 10 mL of benzene at room temperature. The mixture was heated at 80 °C. The mixture was heterogeneous at room temperature but became homogeneous upon being heated. The mixture was made basic with aqueous sodium carbonate solution with ice cooling and extracted with 200 mL of methylene chloride. The extract was dried over anhydrous sodium sulfate, filtered, and concentrated by using a rotary evaporator. The crude product (604 mg, semisolid) was chromatographed on silica gel, and the following compounds were isolated. (a) **6**: 229 mg (38.1%); colorless needles (from methanol); mp 62 °C (lit.[27] 63–64.5 °C) which was identified by comparison with an authentic sample; NMR ($CDCl_3$) δ 7.64–7.10 (7 H, m), 6.74 (2 H, d, J = 8.0 Hz), 3.34 (1 H, s), 1.36 (9 H, s); UV λ_{max} (log ϵ) 285 nm (4.29); mass spectrum, m/e 225 (M^+). Anal. ($C_{16}H_{19}N$): C, H, N. (b) **7**: 40 mg (5.9%); colorless needles (from methanol); mp 48–48.5 °C; NMR ($CDCl_3$) δ 7.36 (5 H, s), 7.20–6.88 (3 H, m), 6.71 (1 H, d of t), 3.80 (1 H, s), 1.30 (9 H, s); UV λ_{max} (log ϵ) 227 (4.34), 310 nm (3.45); mass spectrum, m/e 225 (M^+). Anal. ($C_{16}H_{19}N$): C, H, N. (c) **8**: 66 mg (7.3%); colorless liquid (purified by microsublimation apparatus at 2mmHg and 110 °C); NMR ($CDCl_3$) δ 6.90 (2 H, d, J = 8.9 Hz), 6.50 (2 H, d, J = 8.9 Hz), 3.85 (1 H, s), 1.36 (9 H, s); mass spectrum, m/e 297 (M^+). Exact mass: 297.0653 (calcd for $C_{11}H_{14}NO_3F_3S$: 297.0643). (d) **5**: 150 mg (30%) which was identified by comparison with an authentic sample by IR spectra.

The experiment was repeated by using 199 mg of **5** with (a) a mixture of 2 mL of TFSA and 6 mL of benzene and (b) a mixture of 4 mL of TFSA and 6 mL of benzene. The reaction mixtures were heated at 70 °C until the starting material had almost disappeared monitoring by TLC (ca. 6 h). The products were analyzed by VPC on a 10% SE 30 column using 4-methyldiphenylamine as an internal standard. The yields of the products were (a) 40% for **6**, 7% for **7**, and 24% for **8** and (b) 49% for **6**, 8% for **7**, and 10% for **8**.

TFSA-Catalyzed Reaction of 5 with Toluene. A 500-mg sample of **5** reacted with toluene (25 mL) in the presence of TFSA (5 mL) and TFA (20 mL) in a manner similar to the reaction with benzene at 60 °C for 3 h. The products, separated by silica gel chromatography, were the following: (a) A mixture of **11b**, **12b**, and **13b**: 331 mg (45.7%); VPC (1.5% SE 30) indicated the presence of two products which gave the same mass spectrum by GC–MS on the same column. Part of the mixture was separated by preparative VPC (10% SE 30). The first component was **11b**: colorless liquid; NMR (CCl_4) δ 7.03 (4 H, s), 6.94 (2 H, d, J = 8.4 Hz), 6.58 (2 H, d, J = 8.4 Hz), 3.30 (1 H, s), 2.26 (3 H, s), 1.37 (9 H, s); UV λ_{max} (log ϵ) 268 nm (4.16); mass spectrum, m/e 239 (M^+). Anal. ($C_{17}H_{21}N$): C, H, N. The second component isolated by VPC was a mixture of two compounds which could not be separated by VPC on an SE 30 or OV 17 column. From NMR and the result of the TFSA-catalyzed reaction of **1** with toluene, a mixture of two isomers, i.e., **12b** and **13b**, was obtained: colorless liquid; NMR (CCl_4) δ 7.32–6.98 (6 H, m), 6.66 (2 H, d, J = 8.8 Hz), methyl peaks at 2.36 and 2.32 (total 3 H), 1.35 (9 H, s); mass spectrum, m/e 239 (M^+). Anal. ($C_{17}H_{21}N$): C, H, N. Yields of **11b**, **12b**, and **13b** were 18%, 11%, and 17%, respectively, by NMR methyl peak integration. (b) A mixture of 2-(*N-tert*-butylamino)methylbiphenyls (**14b**): 53 mg (7.3%); VPC on a 1.5% SE 30 column indicated the presence of three isomers which gave the same mass spectrum (m/e 239 (M^+)) by GC–MS. Further separation was not attempted, but these are plausibly three isomers. (c) **8**: 72 mg (8.0%). (d) **5**: 53 mg (10.6%).

TFSA-Catalyzed Reaction of 15b with Benzene. According to a procedure similar to the reaction of **5**, 500 mg of **15b** gave 819 mg of reddish oil. The crude product was separated by silica gel column chromatography. (a) A mixture of **16b**, **17b**, and **18b**: 426 mg (63.7%); GC–MS (1.5% SE 30) indicated the presence of three isomers (m/e 239 (M^+)) which were isolated by preparative VPC (10% SE 30) as pure compounds. The first component was **16b**: colorless liquid; NMR (CCl_4) δ 7.20 (5 H, s), 6.86 (1 H, d, J = 8.1 Hz), 6.56–6.42 (2 H, m), 3.12 (1 H, s), 2.13 (3 H, s), 1.30 (9 H, s); UV λ_{max} (log ϵ) 231 nm (4.30); mass spectrum, m/e 239 (M^+). Compound **16b** was heated with acetic anhydride to give an acetate as colorless needles (from dilute methanol), mp 100–101 °C. Anal. ($C_{19}H_{23}NO$): C, H, N. Although a sufficient amount was not isolated, the second component was **17b**, identified by comparing TLC, VPC, and GC–MS data with those of the major product from the reaction of *N-tert*-butyl-*N*-(3-methylphenyl)hydroxylamine with benzene. The third component was **18b**: colorless liquid; NMR (CCl_4) δ 7.13 (5 H, m), 6.81 (2 H, d, J = 9.0 Hz), 6.50 (2 H, d, J = 9.0 Hz), 3.82 (2 H, s), 3.11 (1 H, s), 1.31 (9 H, s); UV λ_{max} (log ϵ) 242 nm (4.02); mass spectrum, m/e 239 (M^+). Anal. ($C_{17}H_{21}N$): C, H, N. Yields of **16b**, **17b**, and **18b** were 44%, 2.5%, and 17%, respectively. (b) **19b**: 122 mg (18.3%); colorless liquid (purified by microsublimation apparatus at 2mmHg and 120 °C); the UV spectrum suggested that this was a 2-substituted biphenylamine; NMR (CCl_4) δ 7.37–7.16 (5 H, m), 6.88–6.68 (3 H, m), 3.52 (1 H, s), 2.22 (3 H, s), 1.22 (9 H, s); UV λ_{max} (log ϵ) 227 nm (4.23); mass spectrum, m/e 239 (M^+). Anal. ($C_{17}H_{21}N$): C, H, N.

TFSA-Catalyzed Reaction of *N-tert*-Butyl-*N*-(3-methylphenyl)-hydroxylamine with Benzene. According to a similar procedure for **5**, 500 mg of *N-tert*-butyl-*N*-(3-methylphenyl)hydroxylamine, after at 80 °C for 6 h, gave 650 mg of oil on workup. The products were separated by column chromatography on silica gel. (a) **17b**: colorless solid; mp 42–43 °C; NMR (CCl_4) δ 7.18 (5 H, m), 6.86 (1 H, d, J = 8.4 Hz), 6.54–6.38 (2 H, m), 3.30 (1 H, s), 2.16 (3 H, s), 1.34 (9 H, s); UV λ_{max} (log ϵ) 264 nm (4.03); mass spectrum, m/e 239 (M^+). Compound **17b** was heated on a steam bath with acetic anhydride to give an acetate as colorless plates (from dilute methanol), mp. 104–105 °C. Anal. ($C_{19}H_{23}NO$): C, H, N. (b) A mixture of **2-(*N-tert*-butylamino)methylbiphenyls**: 51 mg (7.7%); colorless liquid; GC–MS indicated the presence of two isomers (m/e 239 (M^+)). (c) **3-Methyl-4-((trifluoromethanesulfonyl)oxy)-*N***-

(35) Endo, Y.; Ohta, T.; Shudo, K.; Okamoto, T. *Heterocycles* **1977**, *8*, 367.

tert-butylaniline: 123 mg (14.2%); colorless liquid (purified by microsublimation apparatus at 2mmHg and 100 °C); NMR (CCl_4) δ 6.86 (1 H, d, J = 9.2 Hz), 6.49 (2 H, m), 3.56 (1 H, s), 2.27 (3 H, s), 1.34 (9 H, s); mass spectrum, m/e 311 (M^+). Exact mass: 311.0827 (calcd for $C_{12}H_{16}NSO_3F_3$: 311.0799).

TFSA-Catalyzed Reaction of 1 with Benzene. A 1-mL sample of TFSA was added slowly to an ice-cooled, vigorously stirred mixture of 100 mg of **1** and 3 mL of benzene under nitrogen and stirred additionally for 30 min. After workup, the reaction mixture gave **9** and **10**, which were identified by comparison with authentic samples.

The reaction was repeated by using 100–200 mg of **1** with the conditions shown in Table I. The products were analyzed by VPC (10% SE 30) using phenanthrene as an internal standard. The yields of the products are shown in Table I.

TFSA-Catalyzed Reaction of 1 with Toluene. The procedure was the same as that for **1** with benzene, and from 300 mg of **1**, 18 mL of toluene, and 2 mL of TFSA, 465 mg of reddish oil was obtained. The product was separated by chromatography on silica gel. (a) A mixture of **11a**, **12a**, and **13a**: 201 mg (39.9%); GC–MS on a 1.5% SE 30 column indicated the presence of two isomers (m/e 183 (M^+)). Part of the mixture was separated by preparative VPC (SE 30). The first component was identified as **11a**: colorless liquid; NMR (CCl_4) δ 7.04 (4 H, s), 6.95 (2 H, d, J = 8.0 Hz), 3.43 (2 H, s), 2.26 (3 H, s); UV λ_{max} (log ϵ) 262 nm (4.13); mass spectrum, m/e 183 (M^+). Compound **11a** was heated on a steam bath with acetic anhydride for 1 h to give an acetate as colorless needles (from dilute methanol), mp 146–147 °C (lit.[36] 147 °C). Anal. ($C_{15}H_{15}NO$): C, H, N.

The second component could not be separated by VPC (SE 30, OV 17, and 101) or high-pressure LC; however, NMR showed two methyl peaks, and thus this fraction must be a mixture of two isomers, i.e., **12a** and **13a**. This assignment was confirmed by comparison with authentic samples by IR and NMR spectra: NMR (CCl_4) δ 7.40–6.98 (6 H, m), 6.69 (2 H, d, J = 8.8 Hz), 3.50 (2 H, s), methyl peaks at 2.36 and 2.32 (total 3 H); mass spectrum m/e 183 (M^+); IR (CS_2) 836, 828, 807, 784, 704 cm^{-1}. Pure **13a** was obtained by recrystallization from hexane as colorless flakes: mp 96 °C (lit.[37] 97 °C); NMR ($CDCl_3$) δ 7.36 (2 H, d, J = 8.8 Hz), 7.32 (2 H, d, J = 8.8 Hz), 7.12 (2 H, d, J = 8.8 Hz), 6.69 (2 H, d, J = 8.8 Hz), 3.65 (2 H, s), 2.32 (3 H, s); UV λ_{max} (log ϵ) 279 nm (4.29); mass spectrum, m/e 183 (M^+). Anal. ($C_{13}H_{13}N$): C, H. N. Yields of **11a**, **12a**, and **13a** were 18%, 9%, and 13%, respectively, by NMR methyl peak ratio. (b) A mixture of **2-aminomethylbiphenyls** (**14a**): 115 mg (22.9%); GC–MS on a 1.5% SE 30 column indicated the presence of two isomers (m/e 183 (M^+)); a part was separated by preparative VPC (10% SE 30). UV spectra of the two isomers were consistent with those of the assigned structures. The first component was identified as **2-amino-2′-methylbiphenyl**: colorless solid; mp 36–36.5 °C; NMR (CCl_4) δ 7.12 (4 H, s), 6.91 (2 H, t, J = 8.0 Hz), 6.70 (1 H, d, J = 8.0 Hz), 6.59 (1 H, d, J = 8.0 Hz), 3.29 (2 H, s), 2.15 (3 H, s); UV λ_{max} (log ϵ) 296 nm (3.46); mass spectrum, m/e 183 (M^+). Anal. ($C_{13}H_{13}N$): C, H, N. The second component was identified as **2-amino-4′-methylbiphenyl**: colorless liquid; NMR (CCl_4) δ 7.10 (4 H, m), 6.92 (2 H, t, J = 8.0 Hz), 6.61 (1 H, d, J = 8.0 Hz), 6.50 (1 H, d, J = 8.0 Hz), 3.50 (2 H, s), 2.38 (3 H, s); UV λ_{max} (log ϵ) 227 (4.32), 302 nm (3.52); mass spectrum, m/e 183 (M^+). Anal. ($C_{13}H_{13}N$): C, H, N.

Preparation of 13a. A mixture of 4-iodonitrobenzene (1 mol), 4-iodotoluene (3 mol), and a catalytic amount of copper powder in DMF was refluxed for 6 h. Chromatography of the reaction mixture gave **4-nitro-4′-methylbiphenyl**: colorless needles (from methanol); mp 143.5–144.5 °C (lit.[37] 140 °C); NMR ($CDCl_3$) δ 8.26 (2 H, d, J = 9.0 Hz), 7.70 (2 H, d, J = 9.0 Hz), 7.52 (2 H, d, J = 8.3 Hz), 7.28 (2 H, d, J = 8.3 Hz), 2.40 (3 H, s). Anal. ($C_{13}H_{11}NO_2$): C, H, N. Catalytic hydrogenation of the nitrobiphenyl (Pd/C in ethanol) gave **13a** (colorless flakes (from benzene), mp. 98–99 °C (lit.[37] 97 °C)), which was identical with **13a** from the acid-catalyzed reaction (NMR and IR (CS_2) 836, 807 cm^{-1}).

Preparation of 12a. **3-Methyl-4′-nitrobiphenyl** was prepared from 4-iodonitrobenzene and 3-iodotoluene as above: colorless needles (from methanol and benzene); mp 59–60 °C; NMR ($CDCl_3$) δ 8.22 (2 H, d, J = 9.8 Hz), 7.67 (2 H, d, J = 9.8 Hz), 7.46–7.19 (4 H, m), 2.42 (3 H, s). Anal. ($C_{13}H_{11}NO_2$): C, H, N. Catalytic hydrogenation (Pd/C) gave **12a**: colorless liquid; NMR (CCl_4) δ 7.36 (2 H, d, J = 8.1 Hz), 7.38–6.98 (4 H, m), 6.70 (2 H, d, J = 8.1 Hz), 3.20 (2 H, s), 2.36 (3 H, s); mass spectrum, m/e, 188 (M^+). IR (CS_2) 828, 784, 704 cm^{-1}. Anal. ($C_{13}H_{13}N$): C, H, N.

TFSA-Catalyzed Reaction of 15a with Benzene. This reaction followed the same procedure as the TFSA-catalyzed reaction of **1** with benzene, using 300 mg of **15a**, 18 mL of benzene, and 2 mL of TFSA. After workup, 404 mg of oil was obtained. The crude product was separated by silica gel column chromatography to give the following. (a) **19a**: 167 mg (37.4%); colorless liquid (purified by a microsublimation apparatus at 5mmHg and 130 °C); NMR (CCl_4) δ 7.44–7.20 (5 H, m), 7.02–6.86 (2 H, m), 6.65 (1 H, d, J = 8.6 Hz), 3.42 (2 H, s), 2.28 (3 H, s); UV λ_{max} (log ϵ) 226 (4.37), 308 nm (3.52); mass spectrum, m/e 183 (M^+). The amine was heated on a steam bath with acetic anhydride to give an acetate as small prisms (from dilute methanol), mp 125–126 °C. Anal. ($C_{15}H_{15}NO$): C, H, N. (b) **16a**: 106 mg (23.7%); colorless liquid (purified by microsublimation apparatus at 5mmHg and 130 °C); NMR (CCl_4) δ 7.44–7.14 (5 H, m), 7.01 (1 H, d, J = 8.1 Hz), 6.65–6.44 (2 H, m), 3.44 (2 H, s), 2.14 (3 H, s); UV λ_{max} (log ϵ) 228 (4.35), 300 nm (3.39); mass spectrum, m/e 183 (M^+). The amine was heated on a steam bath with acetic anhydride for 1 h to give an acetate as colorless prisms (from dilute methanol), mp 158–159 °C. Anal. ($C_{15}H_{15}NO$): C, H, N. (c) **18a**: 32 mg (7.1%); colorless liquid (purified by microsublimation apparatus at 3mmHg and a bath temperature of 100 °C); NMR (CCl_4) δ 7.14 (5 H, s), 6.92 (2 H, d, J = 8.0 Hz), 6.56 (2 H, d, J = 8.0 Hz), 3.82 (2 H, s), 3.30 (2 H, s); UV λ_{max} (log ϵ) 241 nm (4.02); mass spectrum, m/e 183 (M^+). The amine was heated on a steam bath with acetic anhydride to give an acetate as colorless flakes (from methanol), mp 131–131.5 °C (lit.[38] 128–129 °C). Anal. ($C_{15}H_{15}NO$): C, H, N.

Deamination of 16a and 18a. The amines **16a** and **18a** were diazotized in the usual manner and reduced to methylbiphenyls. Two methylbiphenyls were identified by comparison with authentic samples[39] by IR spectra and TLC.

TFSA-Catalyzed Reaction of *N*-(3-Methylphenyl)hydroxylamine with Benzene. The procedure was the same as that for the TFSA-catalyzed reaction of **1** with benzene, using 500 mg of *N*-(3-methylphenyl)-hydroxylamine, 16 mL of benzene, and 4 mL of TFSA. After workup, 713 mg of oil was obtained. The crude product was separated by silica gel chromatography to give the following. (a) **17a**: 356 mg (47.7%); colorless liquid (purified by microsublimation apparatus at 2mmHg and bath temperature of 100 °C); NMR (CCl_4) δ 7.24 (5 H, m), 6.98 (1 H, d, J = 8.1 Hz), 6.51 (2 H, m), 3.60 (2 H, s), 2.21 (3 H, s); UV λ_{max} (log ϵ) 264 nm (4.06); mass spectrum, m/e 188 (M^+). The amine was heated with acetic anhydride on a steam bath to give an acetate as colorless needles (from dilute methanol), mp 108 °C. Anal. ($C_{15}H_{15}NO$): C, H, N. (b) **2-Amino-4-methylbiphenyl**: 127 mg (17.0%); colorless liquid (purified by microsublimation apparatus at 2mmHg and 100 °C); NMR (CCl_4) δ 7.30 (5 H, m), 6.86 (1 H, d, J = 8.0 Hz), 6.48 (1 H, d, J = 8.0 Hz), 6.39 (1 H, s), 3.48 (2 H, s), 2.14 (3 H, s); UV λ_{max} (log ϵ) 227 (4.36), 302 nm (3.55); mass spectrum, m/e 188 (M^+). the amine was heated with acetic anhydride to give an acetate as colorless needles (from dilute methanol), mp 146 °C (lit.[40] 145 °C). Anal. ($C_{15}H_{15}NO$): C, H, N. (c) **2-Amino-6-methylbiphenyl**: 30 mg (10.7%); colorless liquid (purified by microsublimation apparatus at 2mmHg and bath temperature of 100 °C); NMR (CCl_4) δ 7.22 (5 H, m), 6.86 (1 H, d, J = 8.0 Hz), 6.50 (1 H, d, J = 8.0 Hz), 6.38 (1 H, d, J = 8.0 Hz), 3.20 (2 H, s), 1.92 (3 H, s); UV λ_{max} (log ϵ) 295 nm (3.30); mass spectrum, m/e 188 (M^+). (d) **3-Methyl-4-((trifluoromethanesulfonyl)oxy)aniline**: 52 mg (5.7%); colorless plates (from benzene and hexane; mp 63.5–64 °C; NMR ($CDCl_3$) δ 6.86 (1 H, d, J = 9.0 Hz), 6.49 (2 H, m), 3.60 (2 H, s), 2.26 (3 H, s); mass spectrum, m/e 255 (M^+). Exact mass: 255.0196 (calcd for $C_8H_8NSO_3F_3$: 255.0175).

TFSA-Catalyzed Reaction of 24 with Benzene. To an ice-cooled, stirred mixture of 3 mL of benzene and 3 mL of TFSA was added 200 mg of **24**. After workup, the crude product was separated by silica gel column chromatography to give pure **9** and **21**. The other products were isolated by preparative VPC (10% SE 30). (a) **9**: identified by comparison with an authentic sample by melting point and IR spectra. (b) **21**: colorless cubic crystals (from methanol); mp 68 °C (lit.[41] 67–68 °C). Compound **21** was identified by comparison with an authentic sample by melting point and IR spectra: NMR ($CDCl_3$) δ 7.61–6.04 (12 H, m), 6.81 (1 H, d, J = 10.0 Hz), 3.16 (2 H, s), mass spectrum, m/e 245 (M^+). Anal. ($C_{18}H_{15}N$): C, H, N. (c) **22**: colorless needles (from hexane); mp 96 °C (lit.[42] 93.5–94.5 °C). Compound **22** was identified by comparison with an independently synthesized sample: NMR ($CDCl_3$) δ 7.13 (11 H, m), 6.70 (2 H, m), 3.26 (2 H, s); mass spectrum, m/e 245 (M^+). Anal. ($C_{18}H_{15}N$): C, H, N. (d) **4-Amino-*p*-terphenyl**: pale yellow flakes (from ethanol); mp 199–200 °C (lit[41] 197–198 °C); the amine was identified with an authentic sample; NMR ($CDCl_3$) δ 7.69 (5 H, s), 7.70–7.32 (6 H, m), 6.68 (2 H, d, J = 8.2 Hz), 3.74 (2 H, s); mass spectrum, m/e 245 (M^+). Anal. ($C_{18}H_{15}N$): C, H, N.

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The experiment was repeated by using 200 mg of **24**, TFSA (30 equiv), and benzene (60 equiv). After workup, the products were analyzed by VPC (1.5% Se 30) using 4-phenylazobenzene as an internal standard. The yields of **9**, **21**, **22**, and **4-amino-*p*-terphenyl** were 42.4%, 17.1%, 2.5%, and 0.3%, respectively.

Preparation of 21. The nitration of *m*-terphenyl with gracial acetic acid, concentrated nitric acid, and fuming nitric acid furnished **4'-nitro-*m*-terphenyl**: pale yellow liquid; NMR ($CDCl_3$) δ 8.24 (1 H, d, J = 9.3 Hz), 7.95–7.16 (12 H, m). Anal. ($C_{18}H_{13}NO_2$): C, H, N. The nitro was reduced by catalytic hydrogenation (Pd/C in ethanol) to an amine having the same IR and NMR spectra as those for **21**.

Preparation of 4-Amino-*p*-terphenyl. 4-Nitro-*p*-terphenyl was prepared from *p*-terphenyl following the same procedure as above: pale yellow needles (from methanol); mp 216–219 °C (lit.[41] 210–214 °C); NMR ($CDCl_3$) δ 8.24 (2 H, d, J = 8.5 Hz), 7.70 (2 H, d, J = 8.5 Hz), 7.66 (5 H, s), 7.64–7.30 (4 H, m). Anal. ($C_{18}H_{13}NO_2$): C, H, N. The nitro was reduced to an amine by catalytic hydrogenation (Pd/C in ethanol) identical with 4-amino-*p*-terphenyl from the acid-catalyzed reaction.

Preparation of 22. This compound was prepared by reductive phenylation of 3-nitrobiphenyl[43] To an ice-cooled, stirred mixture of 3-nitrobiphenyl, benzene (50 equiv), and TFSA (50 equiv) was added zinc dust (6 equiv), and the mixture was stirred for 3 h. After the usual workup, **22** was obtained as a major product.

TFSA-Catalyzed Reaction of *N*-(4-Chlorophenyl)hydroxylamine with Benzene. A 300-mg sample of *N*-(4-chlorophenyl)hydroxylamine was reacted with benzene as described for **24** in the presence of TFSA. After workup, the crude product was separated by silica gel column chromatography to give **9**, **21**, and **23** (X = Cl). The other product identified by GC–MS was **22**. **23**: colorless needles (from methanol); mp 50.5–51.0 °C (lit.[44] 47–50 °C); NMR ($CDCl_3$) δ 7.33 (5 H, s), 7.01 (2 H, m), 6.59 (1 H, d, J = 9.0 Hz), 3.52 (2 H, s); mass spectrum, m/e 203 (M^+). Anal. ($C_{12}H_{10}NCl$): C, H, N. *N*-Acetate: colorless needles (from methanol); mp 122–124 °C (lit.[45] 122.5 °C). Anal. ($C_{14}H_{12}NOCl$): C, H, N.

The reaction was repeated by using 100 mg of *N*-(4-chlorophenyl)-hydroxylamine, benzene (60 equiv), and TFSA (30 equiv), and the products were analyzed by VPC (1.5% SE 30) which showed the presence of 20.5% of **9**, 2.0% of **21**, 1.4% of **22**, and 44.4% of **23** (X = Cl).

Reaction of *N*-(4-Methoxyphenyl)hydroxylamine with Benzene. A 100-mg sample of *N*-(4-methoxyphenyl)hydroxylamine was added to an ice-cooled, stirred mixture of benzene (60 equiv) and TFSA (30 equiv). After workup, the crude product was analyzed by GC–MS and VPC (1.5% SE 30) using 4-phenylazobenzene as an internal standard which showed the presence of 1.6% of **9**, 2.3% of **21**, 3.0% of **22**, and 8.9% of **23** (X = OCH_3). The structure of the last compound was established by NMR and UV spectra.

Reaction of 25 with Benzene. A mixture of 280 mg of **25**, benzene (60 equiv), and TFSA (10 equiv) was stired at 0 °C for 1 h, and the mixture was left at room temperature for 4 h. Ice-cooled aqueous potassium carbonate was added, and the benzene layer was collected, dried and evaporated to give 261 mg of **26** as colorless flakes, mp 121–122 °C. The mother liquor was chromatographed over silica gel, giving **27** (oil, 20 mg (4.8%)) and an additional crop of **26** (32%). Total yield of **26** was 71%. These two compounds were identified by comparison with authentic samples prepared from aminobiphenyls. VPC yield varied in a range of 64–76% for **26** and 4–6% for **27**.

Reaction of 28 with Benzene. A heterogenous mixture of **28** (435 mg), benzene (20 mL), and TFSA (3 mL) was stirred overnight at room temperature. After the usual workup, the reaction products were separated by preparative TLC on silica gel. Compounds **29**, **31**, and **32** were separated and purified by molecular distillation. They were identified by comparison with authentic samples prepared from **16a**, **19a**, and **18a**, respectively, by their IR spectra. The presence of **30** in the reaction product was verified by VPC retention time and GC–MS. Compound **30** was also prepared from the corresponding aminobiphenyl (**17a**). The yields of these products were determined by VPC: **29**, 46%; **30**, 2%; **31**, 8%; **32**, 4%.

Reaction of 25 with Benzene Catalyzed by Trifluoroacetic Anhydride. A solution of **25** (262 mg) in benzene (60 equiv) was allowed to stand or was stirred at 30 °C in the presence of additional (a) TFA (6 equiv), (b) trifluoroacetic anhydride (3 equiv), (c) trifluoroacetic anhydride (3 equiv) and sodium bicarbonate (5 equiv), and (d) TFA (6 equiv) and trifluoroacetic anhydride (3 equiv). After the addition of aqueous potassium carbonate, the benzene layer was separated, dried, and evaporated. The major product in the reactions b, c, and d was 2-(*N*,*N*-dimethylamino)phenol. Compounds **27** and **26** were analyzed by VPC. The yields of **27** and **26** in the reactions a–d were (**27**, **26** (%)): (a) 0, 0; (b) 0.4, 1.3; (c) 0.6, 1.6; (d) 0.8, 6.3.

Acid-Catalyzed Reaction of 33 with Benzene. A 500-mg sample of **33** was added to an ice-cooled, stirred mixture of benzene (15 equiv) and TFSA (7 equiv). After workup, chromatography of the crude product gave 189 mg of **9** and 28 mg of **21**.

The reaction was repeated by using 1 mmol of **33** in the presence of (a) benzene (60 equiv), TFSA (10 equiv), and TFA (20 equiv) and (b) benzene (60 equiv) and TFSA (30 equiv). The crude product was analyzed by VPC (1.5% SE 30) using tetraphenylethane as an internal standard: (a) **9** (31%), **21** (27%), **22** (3%); (b) **9** (47%), **10** (9%), **21** (4%), **22** (1%).

Acid-Catalyzed Reaction of 35 with Benzene. A 100-mg sample of **35** was added to a mixture of TFSA (20 equiv) and benzene (60 equiv). The mixture was heated at 70 °C for 20 h. The crude product was separated by preparative TLC, and **9**, **21**, and **22** were identified.

The reaction was repeated by using 1 mmol of **35**, and the products were analyzed by VPC (1.5% SE 30) using tetraphenylethane as an internal standard.

Acid-Catalyzed Reaction of 36 with Benzene. A 200-mg sample of **36** was added to a mixture of TFA (10 equiv), TFSA (10 equiv), and benzene (20 equiv). The mixture was stirred for 3 days at room temperature. After workup, the products were separated by preparative TLC. Compounds **9**, **21**, **37**, and **36** were identified by comparison with authentic samples.

The reaction was repeated, and the products were analyzed by VPC (1.5% SE 30) using tetraphenylethane as an internal standard.

Preparation of 37. Compound **37** was prepared from **9** and **33**: orange-red plates (from methanol); mp 154–155 °C. Anal. ($C_{18}H_{14}N_2$): C, H, N.

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