

PHENYLATION OF NITROSO-, AZO-, AZOXY-, AND NITROBENZENE.

A VARIETY OF ONIUM-BENZENIUM IONS

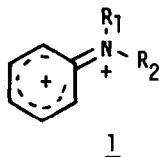
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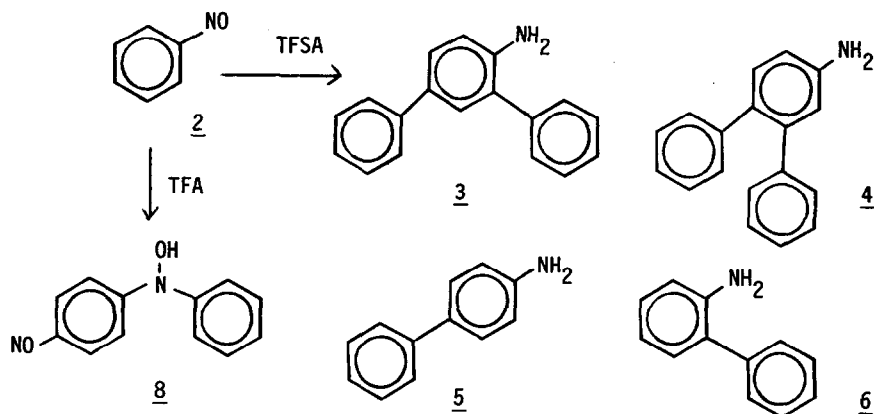
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We have reported that acid-catalyzed reactions of arylhydroxylamines and N,N-dialkyl-aniline-N-oxides with benzene yield 2- and 4-amino (or dialkylamino-)biphenyls.^{1,2} In these reactions we proposed the dicationic intermediates, immonium-benzenium ions (1), where R₁ and R₂ are hydrogen(s) and/or alkyl(s). In the present paper we wish to report several

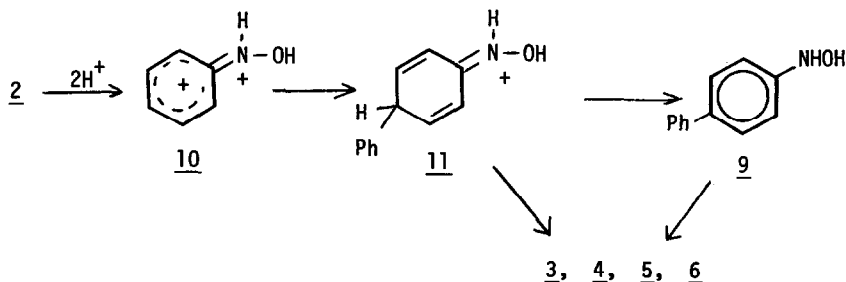


additional reactions which may involve similar intermediates. The bromination of nitrosobenzene and azobenzene has been claimed to involve N-hydroxy- or N-anilinoanilenium ion.³ The protonation in a very strong acid would give dications (1, R₁=H, R₂=OH or NHPH). A similar dicationic intermediate has been postulated in an acid-catalyzed rearrangement of azoxybenzene (the Wallach rearrangement).^{4,5} Thus we have studied the phenylation of nitroso-, azo-, and azoxybenzene as well as nitrobenzene. Early examples of what now can be considered analogous phenylation reactions can be found in the work of Bandrowski,⁶ Kliegl,⁷ and Pummerer,⁸ but generally were given little attention.

Reactions of nitrosobenzene (2) with benzene (60 equiv) in the presence of trifluoromethanesulfonic acid (TFSA, 10 equiv) and trifluoroacetic acid (TFA, 20 equiv) proceeded very rapidly at 0-5°. The products were 4'-amino-m-terphenyl (3, 27%), 4'-amino-o-terphenyl (4, 3%),

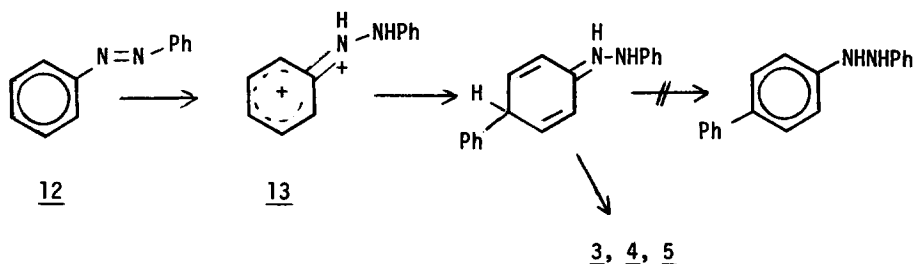


and 4-aminobiphenyl (5, 31%). In the presence of 30 equiv of TFSa, 2-aminobiphenyl (6, 9%), 5 (47%), aminoterphenyls, 3 (4%) and 4 (1%), and diphenylamine (7, 2%) were the products. On the other hand, reaction of 2 in the presence of TFA gave 4-nitrosodiphenylhydroxylamine (8) as reported in earlier papers.⁹ The formation of C-N bond in the presence of TFA agrees with our earlier results on arylhydroxylamines.^{1,10} Therefore the reaction which leads to 3-6 requires the stronger acid, TFSa. These products, 3-6 are also obtained in the reaction of 4-biphenylhydroxylamine (9) with benzene under similar conditions.¹ This suggests that 9 or a closely related species such as 11, is involved in the reaction. The species 11 can be formed by a reaction of N-hydroxyimmonium-benzenium ion 10 and benzene. 10 will be recognized as a diprotonated nitrosobenzene. The formation of aminobiphenyls (5 and 6) from 9 or 11 requires a reduction step, a detail of which is an open one.¹¹

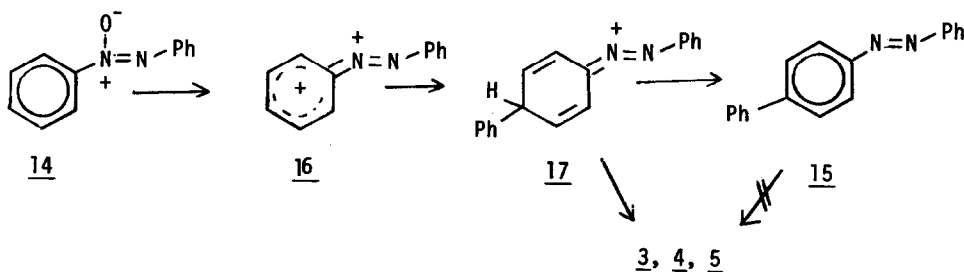


Azobenzene (12), a compound isoelectric with nitrosobenzene, similarly reacts with benzene in the presence of TFSa.¹² The reaction was much slower than the reaction of 2, a higher temperature (80°, 24 hr) being required, and the products were 4-aminobiphenyl (5, 77%), and aminoterphenyls 3 (3%) and 4 (1%).¹³ The net result of the reaction is similar to the reac-

tion of 2. However, the acid-catalyzed reaction of hydrazobenzene gave benzidine instead of aminobiphenyls. Therefore, hydrazobenzene is not a discrete intermediate in the reaction. By analogy with the reaction of 2, the reaction pathway may involve a dicationic species.⁵



The study of azoxybenzene (14) is of particular interest because of the direct analogy with the Wallach rearrangement.⁴ Reaction of 14 with benzene in the presence of TFSA or TFSA-TFA, proceeded smoothly at 40°. ¹² The major product was 4-aminobiphenyl (5, 74%). Aminoterphenyls, 3 (4%) and 4 (1%) were also obtained.^{13b} In addition to these, 4-phenylazobenzene (15) was isolated in 0.5% yield (TFSA-TFA). Formation of 15 is consistent with the Scheme similar to the Wallach rearrangement,^{4b} and naturally interpreted by the reaction of benzene and a dication ⁵ formed by a diprotonation process from azoxybenzene, 14 → 16 → 17 → 15. However, since 15 is stable under the reaction conditions, 15 is not the intermediate which leads to 3,4, and 5. These may be formed from 17 through different pathways. It is quite interesting that the addition of bases (2-4 equiv of potassium salt of TFSA or tertiary amines) increases the yield of 15 to 20%, probably through catalysis of the hydrogen shift or proton abstraction from the intermediate 17.



Finally, nitrobenzene was heated with benzene in the presence of TFSA for 48 hr at 80°. Most of nitrobenzene (77%) was recovered, but aminobiphenyls 5 (37%), 6 (2%), and terphenylamines 3 (9%) and 4 (4%) were obtained.^{13b} Though we can not eliminate a mechanism which involves a prior reduction of nitrobenzene to nitrosobenzene, the 0,0-diprotonated nitrobenzene (1, R₁,R₂=OH) must be considered as an intermediate.

In summary, it is clear that aromatic nitrogen compounds with heteroatoms on the nitrogen atom are susceptible to a nucleophilic attack of benzene under strongly acidic conditions. Despite the insufficient yield, the present result provides an interesting aspect on aromatic reaction and the chemistry of onium-benzenium ions.

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11. The acid-catalyzed reaction of 9 also gave 4-aminobiphenyl as a major product.¹
12. 12, 13, and 15 did not react with benzene in the presence of THF.
13. (a) Yields are based on an equation that a mole of the starting material gives a mole of 4-biphenylamine (and of other products). (b) Yields are based on unrecovered starting materials. Recovery of 12 under the condition was 55%.