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AROMATIC SUBSTITUTION BY N-ARYLHYDROXYLAMINES—II

GENERATION OF NITRENES FROM ARYLHYDROXYLAMINES AND N-BENZENESULFONYLHYDROXYLAMINES AND PHOSPHOROUS PENTOXIDE

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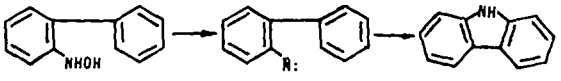
Abstract—Substitution of benzene by N-benzene- and N-(4-methylbenzenesulfonyl)hydroxylamines occurs in the presence of phosphorous pentoxide whereas N-methyl-N-benzenesulfonylhydroxylamine gave no substitution product under the same conditions. When N-(4-methylbenzenesulfonyl)hydroxylamine was treated with phosphorous pentoxide in pyridine, N-(4-methylbenzenesulfonimido)pyridinium ylide was formed. Nitrene intermediates are postulated to account for these products. Similarly carbazole was formed from 2-hydroxylamino[1,1'-biphenyl] and phosphorous pentoxide but with phosphorous pentachloride, 3- and 5-chloro-2-amino[1,1'-biphenyls] were formed, most likely *via* a nitrenium ion intermediate.

In the preceding communication,[1] 8-hydroxylamino-6-methoxyquinoline and 8-hydroxylaminoquinoline could be converted into iminobisquinoline derivatives by a process that has been characterized as an intermolecular aromatic substitution by the aryl nitrene generated from the hydroxylamine by α-elimination of water. The ring N atom was shown to play an important part in the generation of the nitrene intermediate. In this communication we describe our studies of arylhydroxylamines as possible sources of aryl nitrene intermediates.

2-Hydroxylamino[1,1'-biphenyl] (1) contains no possibility for internal participation by base for removal of a proton from the hydroxylamino group and, in this case should the nitrene 2 be generated, carbazole (3) would be formed in a well-documented reaction.[2] Thermolysis of 1 generally gave rise to no less than six and often as many as fifteen or more products, from which carbazole could not be isolated in any significant yield. A TLC method was employed to estimate the yield of carbazole in the various experiments giving not only excellent separations of the six major products, but also imparting a distinctive color to each spot which provided additional proof for identifications (Experimental). In all experiments,[3] including those with added base, only small amounts of carbazole were isolated and it must be concluded that simple heating results in no more than minor amounts of α-elimination at these temperatures. However, when 1 was refluxed in methylbenzene in the presence of phosphorous pentoxide, a 20% yield of carbazole was obtained. Of five other major products, four have been identified by comparison of their distinctive chromatographic characteristics with those of authentic samples prepared separately as 2,2'-azobis-, 2,2'-azoxybis-, 2,2'-hydrazobis- and 2-amino[1,1'-biphenyl]. The product distribution obtained from experiments with phosphorous pentoxide was essentially the same as those from runs without it, except that the amount of carbazole formed increased at the expense of the other products and a small amount of tar was formed (Table 2). Crystalline carbazole could be isolated from these experiments in 10% yield but due to the amount lost during the workup, TLC was more accurate for yield determination.

Reactions carried out at lower temperatures in benzene or diethyl ether gave only slightly lower yields of carbazole (15%); however, a reaction in 1,4-dimethylbenzene at 130° gave only 7·5% of carbazole. Although the yield of carbazole in this reaction was low, the yield of other recognizable products was even lower. Excluding the tarry residue, carbazole was the major product. Thus treatment of the hydroxylamine 1 with phosphorous pentoxide does result in the elimination of water and gives rise to a product which would be expected to be formed by a nitrene. However, alternative mechanisms are possible, especially the formation of a O-phosphate ester which could conceivably yield the carbazole by intermediate nitrene formation, by a concerted process, or by generation of an intermediate nitrenium ion.



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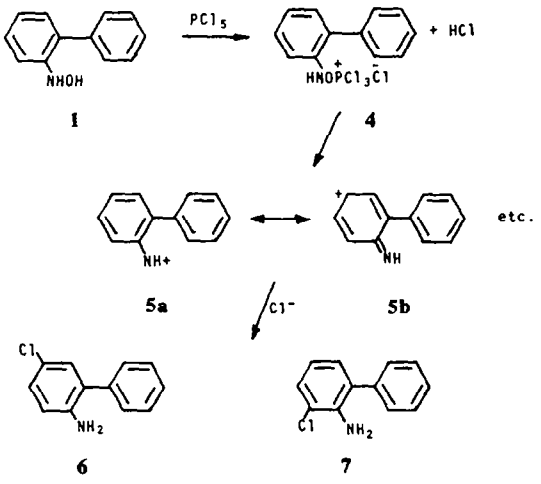
The possibility of nitrenium ion generation is remote for Wenkert and Barnett previously thermolyzed[4] 1 in the presence of sulfuric acid and 4-methylbenzenesulfonic acid under various conditions in unsuccessful attempts to prepare carbazole by a dehydration process. A nitrenium ion should have been generated under those conditions. Additionally, Smith and Brown have thermolyzed[2a] several 2-azidobiphenyls in HBr-acetic acid under conditions expected to generate a nitrenium ion. They found no carbazole formation and ring bromination was the predominant process. This is consistent with the results

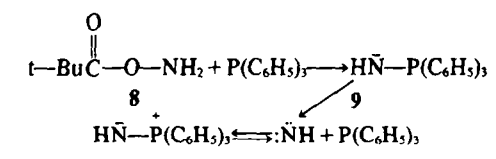
recently reported by Gassman in regard to aryl nitrenium ions.[5]

To obtain evidence that might enable a distinction to be made between a discrete nitrene intermediate or a concerted process, the reaction of arylhydroxylamines with other phosphorous compounds was studied. It has been postulated that treatment of triarylmethylhydroxylamines with phosphorous pentachloride gives rise to a nitrene (Stieglitz reaction[6]). No report of a similar reaction of an arylhydroxylamine is available and, if this type of reaction does generate a nitrene, the reaction of **1** with phosphorous pentachloride would be a good system in which this process could be observed.

When **1** was heated in 4-methylbenzene and phosphorous pentachloride was added, hydrogen chloride was rapidly evolved. After 22 hr at 110°, less than 1% of carbazole was present by TLC. Subsequent workup gave instead two major products, the mass spectrum of each having for its molecular ion *m/e* 203. One was identified as 5-chloro[1,1'-biphenyl]-2-amine (**6**) by preparation of its known acetyl derivative[7] and subsequent hydrolysis to the free amine. The second compound was identified as the corresponding 3-chloro derivative **7** by preparation of its acetyl derivative. This would indicate that the reaction proceeded by the path **4**→**5**→**6**+**7**. Thus either this reaction and the Stieglitz rearrangement proceed by completely different paths or a nitrene is not involved in the Stieglitz rearrangement.



The reaction of hydroxylamines with tervalent phosphorous reagents also has received meager attention. It has recently been reported that the reaction of 0 - 2,2 - dimethyl - 1 - oxopropylhydroxylamine (**8**) with triphenylphosphine gave rise[8] to iminotriphenylphosphorane (**9**). In a compound like **9**, one would expect an equilibrium to exist between it and a nitrene when heated in solution. If a reaction such as this occurred with **1**, it might be possible to prepare carbazole by this route but on reaction with triethylphosphite only a 5% yield of carbazole was formed along with a large number of other products. The reaction was not investigated further, but apparently nitrene formation is not a primary process.

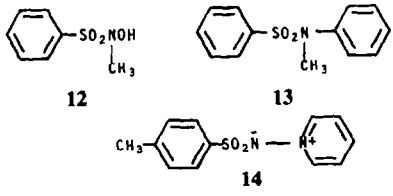


Since intramolecular aromatic substitution by hydroxylamines could be induced by phosphorous pentoxide, it was of interest to investigate whether or not a similar intermolecular reaction would occur. N - (4 - Methylbenzenesulfonyl)hydroxylamine (**10**) (R = Me and N-benzenesulfonylhydroxylamine (**10**) (R = H) were chosen for study for a number of reasons. Firstly, a nitrene generated from **10** (R = Me, H) would be highly electrophilic and would be capable of aromatic substitution, a process which has often been observed in the reactions of sulfonylnitrenes. Secondly, sulfonylhydroxylamines do not undergo intramolecular rearrangements as readily as other hydroxylamines (e.g., carbonyl- or triarylmethylhydroxylamines). Finally, they are stable and readily prepared from the corresponding sulfonyl chloride and hydroxylamine. After **10** (R = Me) had been heated in benzene in the presence of phosphorous pentoxide, a 5% yield of N - phenyl - 4 - methylbenzenesulfonamide (**11**; R = Me) was isolated. A similar reaction of **10** (R = H) in benzene gave **11** (R = H) (6%). Aromatic substitution by sulfonylhydroxylamines has not been described previously and this new reaction is analogous to

10 **11**

the reaction of the corresponding azides which also give **11** (R = Me) and **11** (R = H) when thermolyzed in benzene.[9] As in the reaction of 2 - hydroxylamino[1,1' - biphenyl] (**1**) the mechanism may or may not involve a nitrene, although participation of the aryl substrate seems less likely in the present case than in the reaction of **1** since in the latter it would be an intramolecular process, while in the former, a bimolecular one.

To obtain more information on the nature of the reactive intermediate in this reaction, N - methyl - N - benzenesulfonylhydroxylamine (**12**) was prepared.[10] Should **12** yield **13** upon treatment with phosphorous



pentoxide in benzene, a nitrene mechanism could be discounted. Several reactions of this type were carried out under a variety of conditions, but no detectable amounts of **13** were formed. Thus the intermediacy of a nitrene remains a distinct possibility in the reactions of **10**.

Regarded as a manifestation of the electrophilic character of nitrenes is the addition to an unshared electron pair on phosphorous,[11] sulfur[12] or nitrogen.[13] A number of nitrenes have been intercepted by the use of a solvent containing such a heteroatom and, for this reason, the reaction of **10** (R = Me) in pyridine in the presence of phosphorous pentoxide was examined. The product isolated (11%) was identified as N - (4 - methylbenzenesulfonimido)pyridinium ylide (**14**).

The formation of **14** provides strong support for the suggestion that the dehydration of **10** (R = Me) generates a nitrene by α-elimination. Although evidence is lacking

that pyridine had no effect on the decomposition of **10** it is reasonable that the reaction involves trapping of an initially formed nitrene. This conclusion is consistent with the results obtained from the reactions of **10** (R = Me) and **10** (R = H) in benzene in which no pyridine was present but in which a product expected to be formed from a nitrene was produced.

EXPERIMENTAL*

Thermolysis of 2-hydroxylamino[1,1'-biphenyl] (1)

TCL was developed in order to determine accurately the product distribution in the reactions of **1**. Sample application and development (solvent system: chloroform) were carried out as described previously[1] except that after removal of the plate from the developing chamber, it was treated with HCl. To a 30 cm evaporating dish was added conc. HCl (100 ml). After development, the thin layer plate was placed coated side down into the evaporating dish so that it rested 2–3 cm above the acid. A second evaporating dish was used as a cover. After 10 min, all the spots on the plate had developed intense colors and the plate was removed. In this system, the spot corresponding to carbazole became brilliant azure (Table 1).

Table 1. Thin layer chromatographic data on the products from the decomposition of **1**

Compound	rf value	Color[a]
2,2'-Azobis[1,1'-biphenyl]	0.66	violet
2,2'-Azoxybis[1,1'-biphenyl]	0.57	pale yellow
Carbazole	0.49	azure
2,2'-Hydrazobis[1,1'-biphenyl]	0.39	brown
2-Amino[1,1'-biphenyl]	0.35	green
Unknown	0.28	blue-gray
2-Hydroxylamino[1,1'-biphenyl]	0.25	gray

[a]After development with HCl.

(a) *In methanol.* Compound **1** (100 mg, 0·54 mmole)[4] was heated for 22 hr at reflux in MeOH (10 ml) under N_2. The red soln was then concentrated to an oil *in vacuo* and the residue dissolved in chloroform. Only 1% of carbazole was present by TLC analysis, although all of **1** had undergone reaction.

(b) *In methanol in the presence of pyridine.* **1** (100 mg, 0·54 mmole) was heated under reflux for 22 hr in MeOH (20 ml) under N_2 in the presence of pyridine (0·04 ml, 0·5 mmole). After the usual workup, TLC analysis revealed carbazole (1 ± 1%) and a small amount of unreacted **1**. Thermolysis in a variety of solvents and in the presence of several organic bases resulted in comparable yields of carbazole.

2-Amino[1,1'-biphenyl],[14] 2,2'-hydrazobis[1,1'-biphenyl],[15] 2,2'-azobis[1,1'-biphenyl],[15] and 2,2'-azoxybis[1,1'-biphenyl][15] were all prepared by literature methods.

Reaction of **1** *in the presence of phosphorous pentoxide*

(a) *In methylbenzene.* Compound **1** (100 mg, 0·54 mmole) was added to methylbenzene (10 ml) at 90–95°. P_2O_5 (0·2 g) was then also added with stirring. The undissolved hydroxylamine turned black, as did the appearance of the solvent. The mixture was stirred and refluxed for 22 hr. After this time, the mixture was cooled and quenched with water. After basification to *ca.* pH 8, the mixture was separated from a small amount of tar which was present (0·02 g). The two phases were separated, and the aqueous phase was extracted with chloroform. The organic portions were combined, washed with salt water, and dried with Na_2SO_4. TLC analysis of the soln showed: carbazole (20 ± 5%), 2,2'-azobis[1,1'-biphenyl] (15 ± 5%), 2,2'-azoxybis[1,1'-biphenyl] (*ca.* 5%), 2,2'-hydrazobis[1,1'-biphenyl] (10 ± 5%) and 2-amino[1,1'biphenyl] (10 ± 5%).

This experiment was repeated on a larger scale using 1·0 g of **1**. The yield of carbazole was again found to be 20 ± 5% by TLC. After TLC analysis, the organic solution was washed three times with 10% HCl, then with water. After concentration to an oil, the residue was dissolved in 1,4-dimethylbenzene and charcoaled. The clear soln was cooled at −5° and a solid precipitated. It was separated and found to be mainly carbazole and 2,2'-azoxybis[1,1'-biphenyl] by TLC. A recrystallization from 1,4-dimethylbenzene afforded carbazole: 0·09 g (10%); m.p. 243–244° (lit.[16] m.p. 245°). A second recrystallization gave carbazole with m.p. 245° and an IR spectrum superimposable with that of an authentic sample.

Reaction of **1** *in the presence of phosphorous pentachloride*

The hydroxylamine **1** (0·5 g, 2·7 mmoles) and PCl_5 (0·6 g, 3·0 mmoles) were heated under reflux in methylbenzene (25 ml). As the mixture was warmed, HCl was given off and by the time reflux temp was reached the mixture was very dark. After refluxing for 22 hr the reaction was quenched with water and made slightly alkaline. The layers were separated, and TLC examination of the methylbenzene soln showed *ca.* 1% of carbazole. The methylbenzene soln was washed with 10% HCl. The acid wash was layered with chloroform and made slightly alkaline. The mixture was stirred and the layers were separated. The chloroform soln was dried with Na_2SO_4 and concentrated to an oil. TLC showed the oil to be composed of two major products having R_f values of 0·22 and 0·50 (hexane:ether: :50:50). Preparative TLC afforded the compounds as oils. The mass spectrum of each had a molecular ion at *m/e* 203 and exhibited a chlorine isotope peak *m/e* 205. The base peak of each spectrum was *m/e* 167 (M-Cl).

In separate experiments each of the oils was dissolved in dil HCl. The pH of the soln was adjusted to 6·5 and NaOAc (2·0 g) was added, followed by Ac_2O(2·0 g). After heating with steam for several min, the mixture was made slightly alkaline and extracted with benzene. The benzene soln was concentrated. In the experiment involving the compound with R_f value 0·22, crystallization from aqueous EtOH gave N - acetyl - 5 - chloro[1,1' - biphenyl] - 2 - amine as colorless plates: 0·15 g, m.p. 122° (lit.[7] m.p. 122·5°). When the mixture from the acetylation of the compound with R_f value 0·50 was similarly worked up, one week was required for crystallization to occur, whereupon N - acetyl - 3 - chlor [1,1' - biphenyl] - 2 - amine was obtained as nearly colorless irregular prisms: 0·08 g, m.p. 95° (lit.[7] m.p. 97°).

Each of the acetyl compounds was hydrolyzed by warming with dil. HCl. The acetyl compound with m.p. 122° gave, after crystallization from benzene, 5-chloro[1,1'-biphenyl]-2-amine as yellow irregular prisms: 30 mg; m.p. 51° (lit.[7] m.p. 54°). The free amine from N - acetyl - 3 - chloro[1,1' - biphenyl] - 2 - amine could not be crystallized (the m.p. of 3 - chloro[1,1' - biphenyl] - 2 - amine is 15°).

Reaction of N-*(4-methylbenzenesulfonyl)hydroxylamine* (**10**; R = Me) *with benzene in the presence of phosphorous pentoxide*

P_2O_5 (1·0 g) was stirred vigorously in benzene (20 ml) and the mixture was warmed slowly as **10**[17] (R = Me) (1·00 g, 0·53 mmole) was added in portions over 2 hr. After stirring 1 hr at 50°, the mixture was refluxed for 16 hr. The reaction was quenched with water and 20% KOH aq (20 ml) was added. After removal of a small amount of black solids the layers were separated. The alkaline portion was washed with benzene, then adjusted to pH 6·5 with 10% HCl whereupon a solid separated which was collected and found to be a mixture of 4-methylbenzenesulfonamide and **11** (R = Me) by TLC. Extraction with water (Soxhlet) removed most of the 4-

*All m.ps were determined in capillaries using a Thomas-Hoover Melting Point Apparatus, Model No. 6406H and are corrected. Spectral characteristics were determined on the following instrumentation: IR spectra, Perkin-Elmer Model 337 and 137 spectrophotometers; NMR spectra, Varian T-60 and HA-100 spectrometers using TMS as internal standards; massspectra, JEOL JMS-OISC mass spectrometer, utilizing the direct inlet probe with a source temperature of *ca.* 150°. Details of the chromatographic procedures are found in ref 1. Microanalyses were by Instranal Laboratories, Inc., Rensselaer, New York.

Table 2. Decomposition of 2-hydroxylamino[1,1'-biphenyl] in the presence of phosphorous pentoxide[3]

Solvent[b]	Additive	Temp, °C	RN—NR[c]	$RN^{-}-\overset{+}{N}HR$	Product Distribution[a] Carbazole	RNHNHR	RNH_2	Tar
methyl benzene	-	110	15	30±10	3±1	15	20	0
1,4-dimethyl benzene	P_2O_5 (0.2g)	130	5	1	7.5±2.5	15	5	70
methyl benzene	"	110	15	5	20	10	10	20
benzene[d]	"	80	5	10	15	5	15	20
ether[d]	"	35	5	10	15	10	10	20

[a]Yields (exclusive of tar) were estimated by TLC and are accurate to ± 5% unless noted. [b]2-Hydroxylamino[1,1'-biphenyl] (100 mg) was heated for 22 hrs in 10 ml of solvent. [c]R = 2-[1,1'-biphenyl]. [d]In this reaction 30 ml solvent was used.

methylbenzenesulfonamide and recrystallization from ethanol afforded **11** (R = Me) as colorless needles: 69 mg (5%); m.p., m.m.p. 102–103° (lit.[18] m.p. 103°).

Reaction of N-*benzenesulfonylhydroxylamine* (**10**; R = H) *in benzene in the presence of phosphorous pentoxide*

P_2O_5 (1·0 g) was stirred vigorously in benzene (20 ml) while **10**[19] (R = H) (1·00 g, 0·58 mmole) was added over 2 hr while warming on a steam bath. The dark mixture was refluxed for 18 hr then quenched with water. 20% KOH aq (20 ml) was added. After filtering, the layers were separated and the aqueous portion was washed with benzene then adjusted to pH 6·2 with 10% HCl. The resultant dark solid was collected and the water soluble impurities were removed by extraction (Soxhlet). Recrystallization from aqueous EtOH afforded **11** (R = H) as pale-yellow, irregular prisms. Repeated crystallization from aqueous EtOH afforded colorless prisms: 80 mg (6%); m.p., m.m.p. 110° (lit.[19] m.p. 110°).

Reaction of N-*methyl*-N-*benzenesulfonylhydroxylamine* (**12**) *in benzene in the presence of phosphorous pentoxide*

P_2O_5 (1·0 g) was stirred vigorously in benzene (20 ml) as **12**[10] (1·00 g, 0·53 mmoles) was added. The dark mixture was warmed on a steam bath for 1 hr, then refluxed for 16 hr, after which 20% KOH aq (20 ml) was added. After stirring, filtering, and separating the layers, the benzene portion was washed again with 20% KOH, then washed with water. After drying with Na_2SO_4 no **13** was detectable in the benzene soln by TLC. Several similar experiments were carried out in which: (1) **12** was added at 75°; (2) the mixture was stirred at 25° overnight; (3) the order of adding the P_2O_5 and **12** was reversed. No detectable amounts of **13** were formed in any case.

Reaction of N-(4-*methylbenzenesulfonyl*)*hydroxylamine* (**10**; R = Me *in pyridine*

P_2O_5 (1·0 g) and **10** (R = Me) (1·00 g, 0·53 mmole) were stirred and warmed to 35–40° in pyridine (20 ml). After several min at this temp. the mixture became dark, a brown oil formed, and the P_2O_5 was noted to be sticky. Heating was continued for 2 hr, then water (1 ml) was added and the mixture made neutral with 35% NaOH. The mixture was filtered and the insolubles were washed with pyridine. The pyridine wash and filtrate were combined, and stirred with Darco-X (1·0 g). After filtering and concentrating the soln to *ca.* 10 ml, the residue was cooled at −10°. The brown solid which separated was collected and recrystallized twice from EtOH to give N-(4-methylbenzenesulfonimido)pyridinium ylide as colorless plates: 144 mg (11%); m.p. 212° (lit.[13c] m.p. 210°); IR (KBr) 3150, 1610, 1275 (SO_2), 1135 (SO_2) cm^{-1}; mass spectrum, *m/e* (rel intensity) $M^{+\cdot}$ 248 (73), 184 (32, M-SO_2), 93 (90, M-$CH_3C_6H_4SO_2\cdot$), 91 (100); NMR (CF_3COOD-15%) δ 8·64–8·92 (m, 3, γ and α pyridine protons), 8·07–8·32 (m, 2, β pyridine protons), 7·77 (d, 2, ortho protons, $J_{o,m}$ = 8·5 Hz), 7·52 (d, 2, meta protons), 2·60 (s, 3, CH_3). (Found: C, 57·99; H, 4·88; N, 11·24. Calcd for $C_{12}H_{12}N_2O_2S$: C, 58·04; H, 4·87; N, 11·28%).

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