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Communications

Photochemical Rearrangement of *O*-Phenylhydroxylamine

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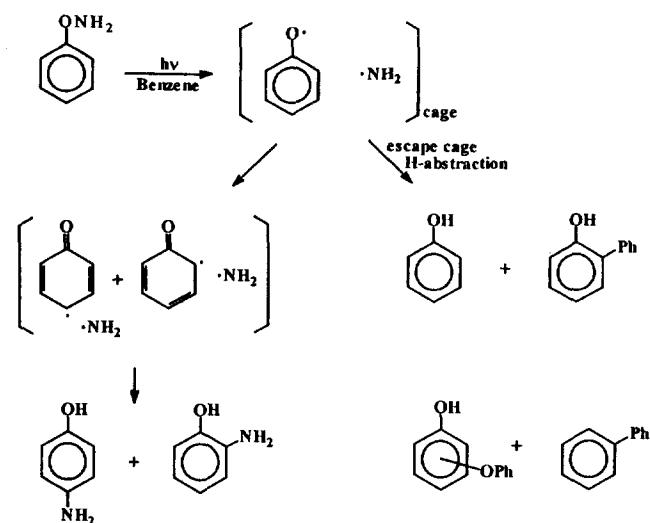
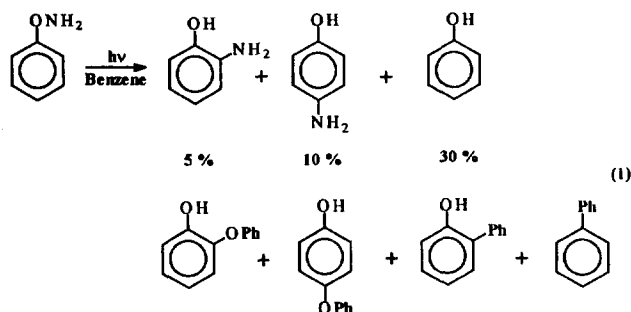
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Chemistry of *O*-phenylhydroxylamine has not been well studied since it was first synthesized by Bungardner and Lilly¹ in 1962. Acid catalyzed rearrangement of *N*-acyl- and *N*-benzoylhydroxylamine was studied by Shudo² *et al.* The acid catalyzed rearrangement is considered to involve concerted [3,3] sigmatropic reactions. Recently, Endo³ studied acid catalyzed reactions of *O*-phenylhydroxylamine, and *N*-phenylhydroxylamine which is known as Bamberger rearrangement. On the other hand, the photochemistry of *O*-phenylhydroxylamine has not been studied. We report photochemical amino-migration of *O*-phenylhydroxylamine.

O-Phenylhydroxylamine was synthesized according to the reports by Krause⁴ and Schudo^{2a}.

Irradiation of *O*-phenylhydroxylamine in benzene at 300 nm afforded phenol as major product, *p*-aminophenol and *o*-aminophenol in a ratio of 2 to 1. Biphenyl, 2-phenylphenol, 2-phenoxyphenol and 4-phenoxyphenol were also obtained⁶ in trace (eq. 1).



Scheme 1.

A detailed mechanism including a responsible excited state is not known at present, however, we propose photo-Fries⁵ type mechanism for amino-migration based on the analysis of the products distribution in different solvent viscosity. Benzene ($C_p=0.56$ at 30 °C) and ethanol ($C_p=1.01$ at 30 °C) are used as a solvent (Scheme 1).

Scheme 1 summarizes the photo-reactions of *O*-phenylhydroxylamine. After absorption of light by $ArONH_2$, a homolytic cleavage of the excited molecules occurs at the O-N bond. The resulting pair of amino and phenoxy radicals would be restrained by a solvent cage until they combine to form rearrangement products and (or) starting material.

Some of the phenoxy radicals in solvent cage would diffuse and eventually abstract hydrogen from solvent to form phenol. Irradiation of *O*-phenylhydroxylamine in ethanol affords 7% of *o*-aminophenol, 14% of *p*-aminophenol and 15% of phenol. In ethanol, compared with benzene, the yields of aminophenols increased with decreasing the yields of phenol. The difference in product distribution between benzene and ethanol may provide cage effect on the formation of phenol and aminophenols. Since the viscosity of ethanol is almost twice of that of benzene, the rate of diffusion out of the solvent

cage should be much slower in ethanol than in benzene.

This solvent cage effect would not only account for the distribution of phenol and aminophenols but would also provide an explanation of formation of biphenyl and diphenylether derivatives. Quenching and emission properties for the detailed mechanism are under investigation.

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- The products, phenol and aminophenols were identified by ¹H NMR, IR and Mass spectra comparing with those of authentic samples. Biphenyl and diphenylether derivatives were identified by comparison of GC retention times and Mass spectra with those of authentic samples.

Synthesis and Characterization of *ortho*-Carborane Substituted Fischer-Type Carbene Complexes 1-[(CO)₅M=C(OCH₃)]-2-R-1,2-closo-C₂B₁₀H₁₀ (M=Cr, W; R=CH₃, C₆H₅)

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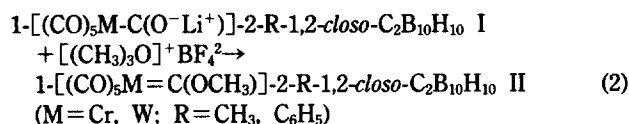
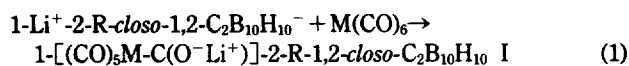
We have studied a series of metal carbene complexes¹ in which the carbene ligand contains a *ortho*-carborane, 1-R-1,2-C₂B₁₀H₁₁, group adjacent to the coordinatively unsaturated carbon atom. Cluster complexes of transition-metals in which the metal atoms are not directly bound are of spe-

cial interest for the evidence they provide the ability of cluster to transmit its influence to the metal. Metal carbene complexes of this type in which metal and carborane are separated by one atom, carbene carbon, could show that some metal-carborane interaction occurs in such compounds.

Although numerous electrophilic transition-metal carbene complexes stabilized by alkyl substituents² are known, simple complexes possessing sterically bulky inorganic analogue are unknown except for the metal carbene complexes in which the carbene ligand contains a ferrocenyl group.³

The addition of organolithium reagents to metal carbonyl complexes is an attractive route metal carbene complexes.⁴ Therefore, a number of *ortho*-carborane substituted carbene complexes of chromium and tungsten were prepared by the reaction of metal carbonyls with *ortho*-carborane lithium reagents. We had hope to prepare *ortho*-carborane substituted carbene complexes of chromium and tungsten and we have been able to prepare such compounds.

When the anionic *ortho*-carborane was treated with metal carbonyl complexes, *α-ortho*-carboranyl metal complexes 1-[(CO)₅M-C(O⁻Li⁺)]-2-R-1,2-closo-C₂B₁₀H₁₀ I were isolated. Subsequent methylation produced desired *ortho*-carboranyl metal-carbene complexes 1-[(CO)₅M=C(OCH₃)]-2-R-1,2-closo-C₂B₁₀H₁₀ II shown in equation 1 and 2.



Each of the complexes was prepared by adaptations of the general methods currently available.⁴ In a typical experiment, a solution of 1-Li⁺-2-R-closo-1,2-C₂B₁₀H₁₀⁻ (R = CH₃, C₆H₅) was prepared^{5,6} by the reaction *in vacuo* of excess *n*-BuLi (4.2 mmol) with 1-R-closo-1,2-C₂B₁₀H₁₁ (3.0 mmol) in tetrahydrofuran (~25 mL) at ~-78 °C. To this solution 3.2 mmol of M(CO)₆ (M = Cr, W) in THF was added with warming from -78 °C to room temperature for 2 h. The solution gradually turned dark brown, suggesting the formation of a metal acyl complex. ¹¹B NMR spectra taken at this point confirmed the exclusive formation of the 1-[(CO)₅M-C(O⁻Li⁺)]-2-R-1,2-closo-C₂B₁₀H₁₀ I. Methylation with (CH₃)₃O⁺BF₄⁻ followed by extraction with hexane gave yellow solid. Subsequent separation was performed on the flash column of silica with hexane to give complexes 1-[(CO)₅M=C(OCH₃)]-2-R-1,2-closo-C₂B₁₀H₁₀ II; (1-[(CO)₅Cr=C(OCH₃)]-2-CH₃-1,2-closo-C₂B₁₀H₁₀ IIa,^{7a} 1-[(CO)₅W=C(OCH₃)]-2-CH₃-1,2-closo-C₂B₁₀H₁₀ IIb,^{7b} 1-[(CO)₅Cr=C(OCH₃)]-2-C₆H₅-1,2-closo-C₂B₁₀H₁₀ IIc,^{7c} 1-[(CO)₅W=C(OCH₃)]-2-C₆H₅-1,2-closo-C₂B₁₀H₁₀ IId.^{7d}

The *α-ortho*-carboranyl carbene complexes of chromium and tungsten are all moderately air stable crystalline solids which are readily soluble in all non-polar solvents (hexane, benzene) and sparingly soluble in polar solvents (ether, acetone). All of these complexes are photo-sensitive but show significant thermal stability in the temperature range of room temperature to 80 °C.

The compound II was produced from rather simple manner shown in equation 3.