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THE REDUCTION OF AROMATIC NITRO AND NITROSO COMPOUNDS BY (BIS(TRIMETHYLSILYL)AMINO)-DIMETHYLPHOSPHINE

JOHN D. BUYNAC, KIRAN P. JADHAV and DEBORAH L. LIVELY

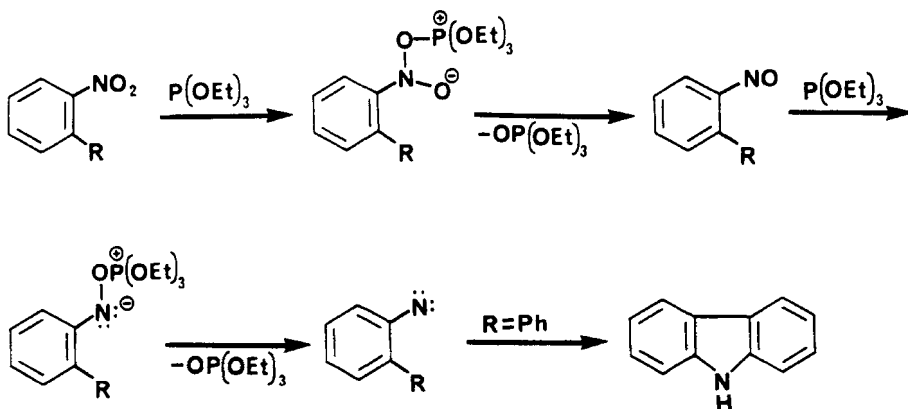
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(Bis(trimethylsilyl)amino)dimethylphosphine is found to deoxygenate both 2-nitrobiphenyl and 2-nitrosobiphenyl to produce carbazole in good yield. In the case of nitrosobenzene, a stable addition compound is formed which suggests a revised mechanism for the reduction of nitro compounds involving the attack of phosphorus at nitrogen.

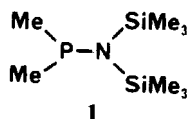
INTRODUCTION

Aromatic nitro and nitroso compounds can be deoxygenated by a variety of tervalent phosphorus reagents.¹ 2-Nitrobiphenyl, for example, on treatment with two equivalents of triethyl phosphite at 130°C for 9 hours will produce carbazole in 82% yield. 2-Nitrosobiphenyl, however, will produce carbazole within 10 minutes when treated with one equivalent of triethyl phosphite at 0°C. Despite extensive work by Cadogan² and others,³ the mechanism of these reductions remains unresolved. The products obtained seem to imply a nitrene or nitrene precursor as an intermediate which undergoes subsequent C—H insertion. Cadogan has proposed a mechanism for the reduction of the nitro group involving initial attack of the phosphorus at oxygen and an intermediate nitroso compound. Direct evidence for any of these intermediates, including the nitrosoaromatic, has not been obtained.

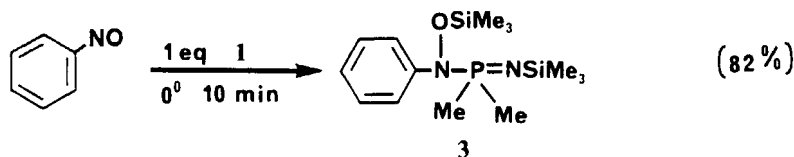
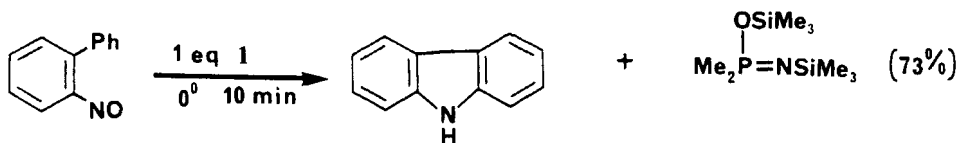
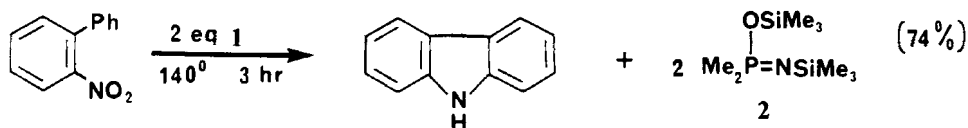


RESULTS AND DISCUSSION

We have had occasion to explore the chemistry of the recently prepared⁴ (bis(trimethylsilyl)amino)dimethylphosphine (**1**). We would like to report our studies of the reactions of **1** with nitro and nitroso aromatics.

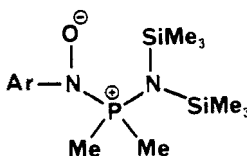


Both 2-nitrobiphenyl and 2-nitrosobiphenyl produce carbazole under similar conditions to those used with triethylphosphite. Instead of the phosphine oxide, the product is *P, P*-dimethyl-*P*-trimethylsiloxy-*N*-trimethylsilylphosphinimine (**2**), probably formed from the rearrangement of the phosphine oxide.⁴ On reaction with nitrosobenzene, however, instead of the expected nitrene insertion products, we observed formation of the stable *P, P*-dimethyl-*N*-phenyl-*N*'-trimethylsiloxy-*N'*-trimethylsilylphosphinimine (**3**).⁵



On reduction of nitrobenzene at 130°, we could detect (by ³¹P NMR) both **2** and **3** formed in a 4 : 1 ratio, respectively. To determine the mechanistic implications of this result, we added nitrosobenzene to **1** while heating at 130°. The same 4 : 1 mixture of **2** and **3** was produced indicating that nitrosobenzene is a viable intermediate in this reduction of nitrobenzene. The phosphinimine **3** may be the

product of an intramolecular silicon transfer from a zwitterion such as **4**, a reaction which has analogy in the chemistry of carbonyl compounds.⁶



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EXPERIMENTAL

Reaction of (bis(trimethylsilyl)amino)dimethylphosphine (**1**) with 2-nitrobiphenyl. In a dry pressure tube, equipped with septum inlet, was prepared a slurry of 2-nitrobiphenyl (1.99 g, 10 mmol) and **1** (5.1 mL, 4.77 g, 22 mmol) under argon. The tube was then placed in an oil bath and heated to 140°C for 3 hours. Workup was accomplished by removing the relatively volatile phosphinimine **2** by vacuum distillation (bp = 53–55° at 3.5 mm) and purifying the remaining material by column chromatography (10% EtOAc/CH₂Cl₂) on silica gel to yield 1.24 g (74%) carbazole.

Reaction of (**1**) with nitrosobenzene. To a chilled (ice bath) solution of nitrosobenzene (3.21 g, 30 mmol) in CH₂Cl₂ (13 mL) was added **1** (6.32 mL, 6.00 g, 27 mmol) dropwise under argon. The reaction mixture was then allowed to warm to room temperature over the course of one hour. The solvent was then removed under vacuum and the product distilled (bp = 105–107°C at 0.4 mm Hg) to yield 6.59 g (82%) **3**.

ACKNOWLEDGMENT

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3. R. J. Sundberg, *J. Am. Chem. Soc.*, **88**, 3781 (1966); P. K. Brooke, R. B. Herbert and F. G. Holliman, *Tetrahedron Letters*, 761 (1973).
4. J. C. Wilburn and R. H. Neilson, *Inorg. Chem.*, **17**, 2519 (1977).
5. IR (neat)_{max} 1595, 1325, 1285, 1250, 850 cm⁻¹; ¹H NMR (CDCl₃) = 0.05 (s, 9 H, NSiMe₃), 0.15 (s, 9 H, OSiMe₃), 1.5 (d, 6 H, *J*_{PH} = 14 Hz, P—CH₃), 7.1–7.5 (m, 5 H, Ar—H); ¹³C NMR (CDCl₃, ¹H decoupled) = -0.3 (s, OSiMe₃), 3.5 (d, *J*_{PC} = 3.7 Hz, NSiMe₃), 15.1 (d, *J*_{PC} = 84 Hz, P—CH₃), 123.1 (d, *J*_{PC} = 3.6 Hz, *m*-C), 124.8 (d, *J*_{PC} = 2.6 Hz, *p*-C), 127.7 (d, *J*_{PC} = 2.5 Hz, *o*-C), 145.5 (d, *J*_{PC} = 2.6 Hz, *ipso*-C); ³¹P NMR (CDCl₃, ¹H decoupled) = 27.2 (s); Anal. Calcd. For C₁₄H₂₉N₂OPSi₂: C, 51.18; H, 8.90; N, 8.53; P, 9.43. Found: C, 51.14; H, 8.19; N, 8.51; P, 9.53).
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