

The red eluate yielded 175 mg (81%) of di-1-azulyl sulfone (**3**): red crystals; mp 187–188°; uv max (CHCl₃) 276 mμ (log ε 4.67), 296 (4.57), 306 (4.53), 366 (4.09), and 381 (4.10); visible max 541 mμ (log ε 2.95) and a shoulder at 625 (2.45); ir (CHCl₃) 7.72 and 8.93 μ (SO₂); nmr τ 0.55 (d, *J* = 10 Hz, H-8), 1.58 (d, *J* = 10 Hz, H-4), 1.62 (d, *J* = 4 Hz, H-2), 2.72 (d, *J* = 4 Hz, H-3) and 2.0–2.7 (m, H-5, H-6, and H-7).

Anal. Calcd for C₂₀H₁₄SO₂: C, 75.44; H, 4.43; S, 10.07. Found: C, 75.41; H, 4.42; S, 9.79.

Registry No.—1, 19254-87-6; 2, 19254-88-7; 3, 19254-89-8.

The Reduction of Nitroso Compounds with Diborane

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Received October 22, 1968

In continuation of our studies of the reduction of unsaturated nitrogen functions with diborane,¹ we are now reporting the results with aromatic nitroso compounds, *gem*-nitronitroso, *gem*-chloronitroso, and *gem*-nitrooximino compounds.

The reduction of aromatic nitroso compounds catalytically or with atomic hydrogen to amines is well documented in the literature.² Treatment of *p*-nitrosophenol with sodium borohydride led to *p*-aminophenol (42%);³ however, nitrosobenzene itself was reduced to azoxybenzene in 73% yield.³

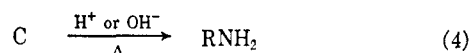
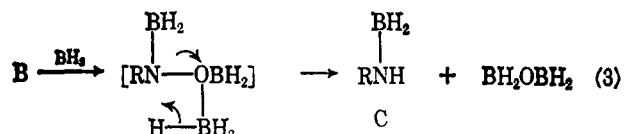
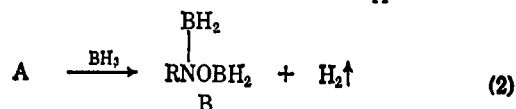
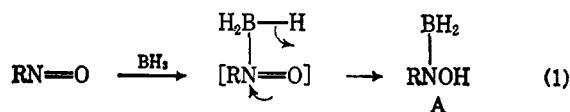
As shown by representative examples in Table I, the reduction of aromatic nitroso compounds with diborane at 25° afforded the corresponding amines in good yields. It is of interest to point out that while *p*-nitroso-*N,N*-dimethylaniline was reduced to 1-amino-4-dimethylaminobenzene in 64% yield, the product of reduction with lithium aluminum hydride was 4,4'-azobis(*N,N*-dimethylaniline) (80%).⁴

In general the reactions were found to be highly exothermic, and 1 equiv of hydrogen was evolved immediately after the addition of diborane, although no acidic hydrogen was present in the starting material. Hydrogen evolution was also observed by Boyer and Ellzey³ when *o*-dinitrosobenzene was treated with sodium borohydride.

By employing nitrosobenzene (**1**) as a model compound, it was found that the yield of amine was, over a wide range, independent of the amount of hydride ion per mol of **1**.⁵

On the basis of quantitative measurements of hydride consumption (3 equiv of hydride ion were consumed in the reduction, 1 equiv of which was evolved as hydrogen prior to hydrolysis) it is proposed that the reduction of

aromatic nitroso compounds with diborane involves essentially four steps (eq 1–4).

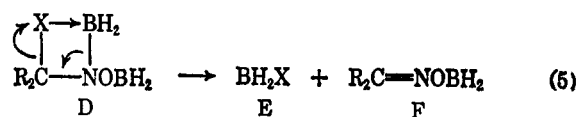


Although intermediates A, B, and C are represented as monomeric, it is quite possible that they are polymeric in nature. The electrophilic attack of diborane on nitrogen in step 1 explains the formation of a hydroxyl group in intermediate A by a four-centered hydride transfer. In step 2, the electrophilic attack on the hydroxyl proton⁶ is supported by the fact that hydrogen was evolved during the reaction prior to hydrolysis. The possibility of the formation of a hydroxylamine intermediate such as B is based on our findings that phenylhydroxylamine was readily reduced by diborane to aniline (65%) at 25°. The remaining steps 3 and 4 are similar to those proposed for the reduction of oxime ethers with diborane.¹

A recent report by Exner,⁸ that 1,1-nitronitrosocyclohexane (**2**) was converted into cyclohexanone oxime (79%) at 15° on treatment with lithium aluminum hydride, prompted us to investigate the reaction of *gem*-nitronitroso compounds with diborane. It was found that the reaction of **2** with diborane at 25° gave the hydroxylamine, *N*-cyclohexylhydroxylamine, in 71% yield. As shown in Table II similar results were obtained with 2,2-nitronitrosopropane (**3**), 1,1-chloronitrosocyclohexane (**4**), and 1-nitropropanal oxime (**5**).

It was established that in these reactions the nitro and chloro groups were eliminated in the reduction, for the hydrolysates of the reaction mixtures gave positive tests for these ions.

Our observations that, as in the case of aromatic nitroso compounds, hydrogen was evolved prior to hydrolysis and that the same amount of hydride was consumed makes it very likely that steps 1 and 2 also apply to the reduction of compounds **2–5**. However, the important difference lies in the elimination step which leads to an oxime intermediate F (eq 5). Further



reaction of F with diborane and subsequent hydrolysis would lead to the hydroxylamine.⁹

(1) For previous publications, see H. Feuer and D. M. Braunstein, *J. Org. Chem.*, **34**, 1817 (1969).

(2) P. A. S. Smith, "The Chemistry of Open Chain Organic Nitrogen Compounds," Vol. II, W. A. Benjamin, Inc., New York, N. Y., 1966, p 375.

(3) J. H. Boyer and S. E. Ellzey, Jr., *J. Amer. Chem. Soc.*, **82**, 2525 (1960).

(4) H. I. Schlesinger and A. E. Finholt, U. S. Patent 2,576,311 (1951); *Chem. Abstr.*, **46**, 2716 (1952).

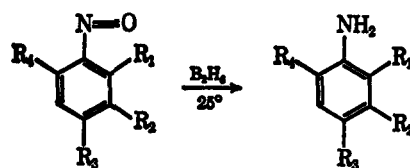
(5) The reduction of **1** with 3.5 and 8.0 equiv of hydride ion gave aniline in yields of 73.8 and 74.2%, respectively.

(6) A. B. Burg and H. I. Schlesinger, *J. Amer. Chem. Soc.*, **55**, 4020 (1933).

(7) It was previously found that the reduction of aliphatic hydroxylamines to amines with diborane required a temperature range of about 105–110°.¹

(8) O. Exner, *Chem. Listy*, **51**, 2055 (1957).

(9) H. Feuer, B. F. Vincent, Jr., and R. S. Bartlett, *J. Org. Chem.*, **30**, 2877 (1965).

TABLE I
 DIBORANE REDUCTION OF AROMATIC NITROSO COMPOUNDS TO AMINES^{a,b}


Amine ^c				Registry no.	Mp or bp (mm), °C	n _D ²⁰	Yield, %
R ₁	R ₂	R ₃	R ₄				
H	H	H	H	586-96-9	75 (14)	1.5858	79.2
CH ₃	H	H	CH ₃	19519-71-2	96-98 (15)	1.5593	84.6
H	CH ₃	H	CH ₃	17075-25-1	99-100 (14)	1.5587	80.5
CH ₃	H	H	H	611-23-4	84-86 (15)	1.5695	89.8
Cl	H	H	H	932-33-2	40-41 (15)	1.5869	73.2
H	H	Cl	H	932-98-9	71-72		71.3
Br	H	H	H	19519-75-6	39-40 (0.1)	1.5793	62.4
H	H	N(CH ₃) ₂	H	138-89-6	51-52		63.7

^a Reactions were carried out for 20 hr at 25°. ^b Hydride consumption measurements indicated that approximately 3 equiv of hydride ion per mole of nitroso compound was consumed, 1 equiv of which was evolved as hydrogen *prior* to hydrolysis. ^c These compounds were identified by their physical data which were in agreement with those reported in the literature.

 TABLE II
 DIBORANE REDUCTION OF *gem*-NITRONITROSO AND *gem*-CHLORONITROSO COMPOUNDS^{a,b}

Compounds	Hydroxylamine ^c	Mp, °C	Yield, %
2,2-Nitronitrosopropane	N-Isopropylhydroxylamine	84-86	65.2
1,1-Nitronitrosocyclohexane	N-Cyclohexylhydroxylamine	140-142	71.0
1-Nitropropanal Oxime	N-Propylhydroxylamine	42-43	71.3
1,1-Chloronitrosocyclohexane	N-Cyclohexylhydroxylamine	140-142	61.7

^a Reactions were carried out for 20 hr at 25°. ^b Hydride consumption measurements indicated that approximately 3 equiv of hydride ion had been consumed per mole of nitroso compound, 1 equiv of which was evolved as hydrogen *prior* to hydrolysis. ^c These compounds were identified by their physical data which were in agreement with those reported in the literature.

The formation of BH₂X is supported by the findings of Binger and Koster,¹⁰ and Brown, *et al.*,¹¹ who have reported that the reaction of 1-chloropropene with diborane afforded a mixture consisting of 1- and 2-propanol arising from the hydroboration of propene after the elimination of BH₂Cl. Recently, Pasto¹² has proposed that elimination could occur with any heteroatom having one or more pairs of nonbonded electrons.

Experimental Section

All apparatus, reagents and equipment are similar to those previously described.^{1,9} All of the nitroso compounds were prepared by methods described in the literature.

Reaction of Diborane with Aromatic Nitroso Compounds.—The following experiment is typical of the procedure employed. To 2.83 g (20.0 mmol) of *p*-chloronitrosobenzene in 30 ml of THF at 0° was introduced by means of a hypodermic syringe 91.0 mequiv of hydride ion, at such a rate that the temperature did not exceed 10°. Continuing the reaction for 20 hr at ambient temperatures, cautiously adding 4 ml of water at 0°, followed by 10 ml of 20% potassium hydroxide, refluxing the reaction mixture 1 hr, extracting with pentane for 24 hr, and removing the solvent *in vacuo* gave after recrystallization from hexane 1.82 g (71.3%) of *p*-chloroaniline: mp 71–72°;¹³ ir (KBr) 3534 and 3436 cm⁻¹ (NH₂); nmr (CDCl₃) δ 3.70 (s, 2, NH₂), 6.70, and 7.30 (q, 4, aromatic H).

Similarly, treating 2.83 g (20.0 mmol) of *p*-chloronitrosobenzene with 91.0 mequiv of hydride ion and keeping the reaction mixture 20 hr at ambient temperatures resulted in the evolution of 20.22 mmol of hydrogen.

Hydrolyzing the reaction mixture at 0° by the cautious addition

of 4 ml of water followed by 10 ml of 20% potassium hydroxide, and refluxing for 1 hr gave an additional 27.35 mmol of hydrogen. The total amount of hydrogen evolved was 47.57 mmol, indicating that 2.17 equiv of hydride ion per mole of nitroso compound was consumed in the reduction; in addition 1.02 equiv of hydride ion was used up as hydrogen *prior* to hydrolysis.

Reaction of Diborane with 1,1-Nitronitrosocyclohexane.—The following experimental procedure employed is typical of the reduce *gem*-nitronitroso, *gem*-chloronitroso, and *gem*-nitrooximino compounds. To 3.14 g (19.9 mmol) of 1,1-nitronitrosocyclohexane in 30 ml of THF at 0° was introduced by means of a hypodermic syringe 91.0 mequiv of hydride ion, at such a rate that the temperature did not exceed 10°. Continuing the reaction for 20 hr at ambient temperatures, cautiously adding 4 ml of water at 0°, and then 10 ml of 20% potassium hydroxide was followed by refluxing the reaction mixture for 1 hr. Extracting with pentane for 24 hr, and removing the solvent *in vacuo* gave after recrystallizing from pentane 1.32 g (57.6%) of *N*-cyclohexylhydroxylamine: mp 140–141°;¹⁴ ir (Nujol) 3280 and 3125 cm⁻¹ (NHOH); nmr (CDCl₃) δ 1.30 [m, 6, (CH₂)₂], 1.80 [m, 4, (CH₂)₂CHNHOH], 2.90 (m, 1, CHNHOH), and 6.08 (s, 2, NHOH).

Similarly treating 3.14 g (19.9 mmol) of 1,1-nitronitrosocyclohexane with 91.0 mequiv of hydride ion and keeping the reaction mixture 20 hr at ambient temperatures resulted in the evolution of 20.70 mmol of hydrogen.

Hydrolyzing the reaction mixture at 0° by the cautious addition of 4 ml of water followed by 10 ml of 20% potassium hydroxide, and refluxing for 1 hr gave an additional 26.70 mmol of hydrogen. The total amount of hydrogen evolved was 47.40 mmol, indicating that 2.17 equiv of hydride ion per mole of nitroso compound was consumed in the reduction; in addition 1.05 equiv of hydride ion was used up as hydrogen *prior* to hydrolysis.

Reaction of Diborane with Phenylhydroxylamine.—The same procedure was followed as in the reduction of aromatic nitroso compounds. From 2.0 g (18.4 mmol) of phenylhydroxylamine¹⁵

(10) P. Binger and R. Koster, *Tetrahedron Lett.*, 156 (1961).

(11) (a) H. C. Brown and K. A. Kebly, *J. Amer. Chem. Soc.*, **86**, 1791 (1964); (b) H. C. Brown and E. Knights, *ibid.*, **90**, 4439 (1968).

(12) D. J. Pasto and J. L. Miesel, *ibid.*, **85**, 2118 (1963).

(13) F. Beilstein and Ap. Kurbatow, *Ann.*, **176**, 27 (1875).

(14) G. Vavon and A. L. Berton, *Bull. Soc. Chim. Fr.*, **37**, 301 (1925).

(15) E. Bamberger, *Chem. Ber.*, **27**, 1548 (1894).

and 102 mequiv of hydride ion there was obtained crude **aniline** which was converted into the **phenylthiourea derivative** in 64.5% yield by treatment with phenyl isothiocyanate:¹⁶ mp 155–156°;¹⁷ nmr (CDCl₃) δ 7.53 (s, 10, aromatic H) and 8.40 (s, 2, NH).

Similarly treating 1.90 g (17.4 mmol) of phenylhydroxylamine with 120 mequiv of hydride ion and keeping the reaction mixture 20 hr at ambient temperatures resulted in the evolution of 33.74 mmol of hydrogen.

Hydrolyzing the reaction mixture at 0° by the cautious addition of 4 ml of water followed by 10 ml of 20% hydrochloric acid and refluxing for 1 hr gave an additional 68.10 mmol of hydrogen. The total amount of hydrogen evolved was 101.84 mmol, indicating that 1.04 equiv of hydride ion per mole of hydroxylamine was consumed in the reduction.

Registry No.—Diborane, 16970-81-3; 2,2-nitrosopropane, 5275-46-7; 1,1-nitronitrosocyclohexane, 14296-14-1; 1-nitropropanal oxime, 19519-78-9; 1,1-chloronitrosocyclohexane, 695-64-7.

Acknowledgment.—We wish to extend our appreciation to the Office of Naval Research for financial support of this work.

(16) N. D. Cheronis and J. B. Entrikin, "Identification of Organic Compounds," Interscience Publishers, New York, N. Y., 1963.

(17) H. Fry, *J. Amer. Chem. Soc.*, **35**, 1539 (1913).

New Synthesis of 1,2-Phenanthrenequinone

HANS-DIETER BECKER

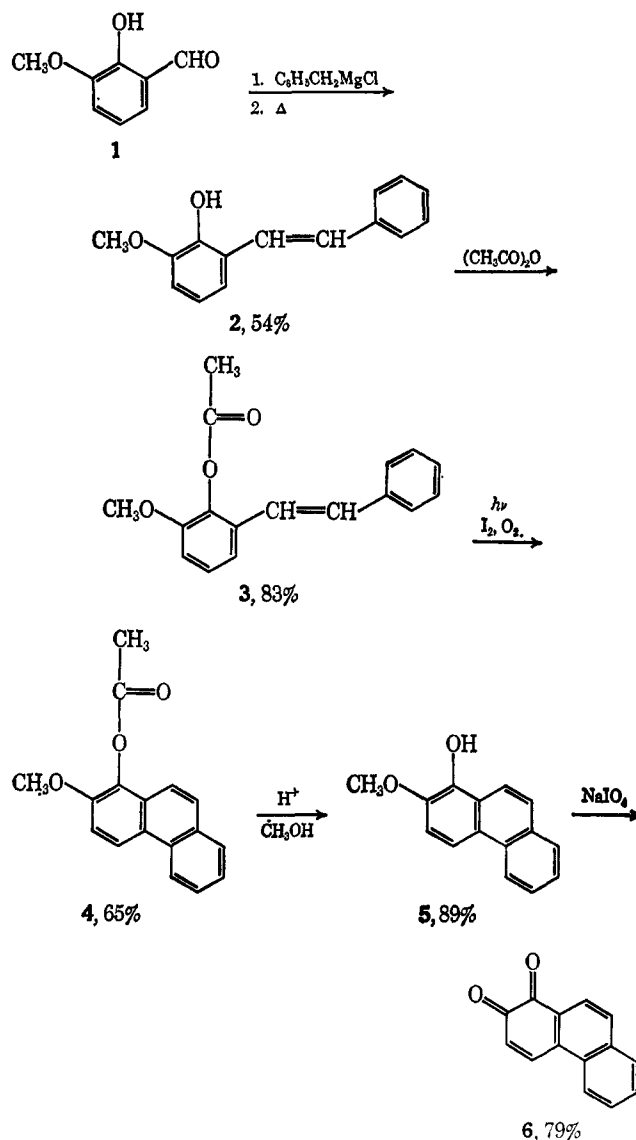
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Received October 4, 1968

The synthesis of 1,2-phenanthrenequinone described by Fieser¹ in 1929 involves the sulfonation of phenanthrene, separation of phenanthrene-2-sulfonic acid *via* its barium salt, and alkali fusion to give 2-phenanthrol. Coupling with diazotized sulfanilic acid followed by reduction leads to 1-amino-2-phenanthrol which upon oxidation with chromic acid yields 1,2-phenanthrenequinone. According to a more recent procedure, 2-phenanthrol can be converted directly into 1,2-phenanthrenequinone by oxidation with potassium nitrosodisulfonate, but no yield has been reported.² The optimal yield of 2-phenanthrol from phenanthrene, however, appears to vary between 13 and 20%.^{3,4}

We have now found that 1,2-phenanthrenequinone can easily be prepared from *o*-vanillin according to a reaction sequence outlined in Scheme I. The previously described reaction of benzyl magnesium chloride with *o*-vanillin (1) followed by dehydration gives 2-hydroxy-3-methoxystilbene (2).⁵ Photolysis of its acetate 3 leads to 1-acetoxy-2-methoxyphenanthrene (4). Acid catalyzed hydrolysis gives 1-hydroxy-2-methoxyphenanthrene (5) which upon oxidation with sodium

SCHEME I THE SYNTHESIS OF 1,2-PHENANTHRENEQUINONE FROM *o*-VANILLIN



periodate⁶ yields 1,2-phenanthrenequinone (6) in a high state of purity. It was characterized by its reduction to 1,2-dihydroxyphenanthrene, which in turn was converted into the diacetate.

Interestingly, the synthesis of 1-hydroxy-2-methoxyphenanthrene (5) has been accomplished a few years ago by the following classical route.⁷ Elbs persulfate oxidation of 2-phenanthrol led to 2-hydroxy-1-phenanthryl sulfate. Methylation with diazomethane followed by acid-catalyzed hydrolysis gave 5 in an over-all yield of about 2.8%. According to the new procedure, the over-all yield of 5 based on *o*-vanillin, however, is approximately 25%. The preparative usefulness of the photochemical route to phenanthrols is thus apparent.

Experimental Section

Melting points were taken on a hot-stage microscope and are not corrected. All analyses were carried out by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

The photolysis was carried out in an immersion well apparatus.⁸

(1) L. F. Fieser, *J. Amer. Chem. Soc.*, **51**, 1896 (1929).

(2) B. Lukowczyk, *J. Prakt. Chem.*, **8**, 372 (1959).

(3) L. F. Fieser, *J. Amer. Chem. Soc.*, **51**, 2460 (1929).

(4) W. O. Foye, M. Weitzenhoff, and A. M. Stranz, *J. Amer. Pharm. Assoc., Sci. Ed.*, **41**, 312, (1952).

(5) E. Adler and K. Lundquist, *Acta Chem. Scand.*, **17**, 13 (1963).

(6) E. Adler, I. Falkegag, and B. Smith, *ibid.*, **16**, 529 (1962).

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