cellent[4] correlation against σ^+ and satisfactory (but improved) correlation against σ. *Thus, mere inclusion of meta substituents may not always provide an easy distinction between valid correlations with σ or σ^+.*

Another interesting example of the problem is seen in the sulfuric acid catalyzed protodesilylation reaction of substituted benzenes[9b] (Table I, entries 5 and 6). Deletion of one substituent (identified by use of Figure 1 and a straight edge) affords a data set of 11 points (3 meta) which provide equally excellent[4] correlations with either σ or σ^+. Similar but less dramatic trends are seen for the perchloric acid catalyzed reaction[9c] (Table I, entries 7 and 8).

The Beckmann rearrangement of substituted acetophenones[9d] was shown by Brown[10] to correlate with σ^+. In fact, the data correlate better with σ than with σ^+ (Table I, entry 9). Deletion of one data point (located with Figure 1 and a straight-edge) improves the correlation against σ^+ to approximately the same level as σ. Interestingly, the point deleted is *p*-OMe, the very one which Exner[8] indicated should be included to decide on a correlation with σ^+. The poor showing of the Beckmann rearrangement data against σ^+ was explained by Pearson to be a result of incorrect σ^+ constants for alkyl groups.[11] He had earlier defined a set of constants for electrophilic reactions, which differ from the σ^+ constants most markedly for the alkyl groups.[9d] Brown ascribed the absence of large deviations from the regression line against σ as being due to the absence of any meta substituents in the data set.[10]

Two reactions which appear to be at the extremes for the magnitude of ρ are $GaBr_3$-catalyzed Friedel–Crafts ethylation and uncatalyzed bromination of substituted benzenes[1d] (Table I, entries 11–14). The reaction constant for the ethylation reaction of −2.4 (vs. σ^+) indicates a small substituent effect. The 11 substrates studied (Table I, entry 11) give a σ/σ^+ correlation coefficient of 0.952, and the rate data correlate satisfactorily[4] against both σ and σ^+. At the other end of the reaction constant scale is the uncatalyzed bromination, the textbook[2] example of differentiating correlations with σ and σ^+. In both articles presenting the σ^+ correlation,[1c,d] large differences in correlation coefficient were observed (Table I, entries 12 and 13). However, from the data a set of nine substituents may be selected (including two meta) with the use of Figure 1 and a straight edge, which afford a reasonably good σ/σ^+ correlation (Table I, entry 14). The correlation of rates against σ^+ improves from satisfactory[4] to excellent, while the correlation against σ improves from no correlation to fair.[4]

The importance of substituent selection appears to increase as the reaction, constant, ρ, decreases. The σ/σ^+ correlations for several entries in Table I are the same (0.951 ± 0.001 for entries 2, 5, 7, 9, 11, and 14). For these entries, Δr increases approximately with ρ and ρ^+ through the series (entry number) 9, 11, 5, 7, 2, 14.

In conclusion, the graphic presented in Figure 1 is a valuable tool in selecting appropriate substituents for an LFER study in which discernment of an electron-deficient conjugated transition state is desired. Substituents should be selected which provide poor σ/σ^+ correlations, especially if a small reaction constant is expected.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the University of Miami Research Council for support of this work.

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Preparation of 1,3,5-Triaminobenzene by Reduction of Phloroglucinol Trioxime

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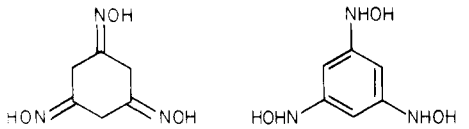
1,3,5-Triaminobenzene or its triacyl derivatives (**5**) have been prepared by catalytic hydrogenation of 1,3,5-trinitrobenzene with palladium on carbon[1] or Raney nickel[2] as catalysts. Since phloroglucinol trioxime (**1**) is nonexplosive and readily available, we have explored the reduction of **1** as a route to 1,3,5-triaminobenzene. Catalytic hydrogenation of **1** with Raney Ni in *n*-butyl acetate is a convenient method for preparing 1,3,5-triaminobenzene in high yield. Pd/C also catalyzes the hydrogenation of **1** in the presence of acetic anhydride to give **5**, in somewhat lower yield. Zinc in acetic acid/acetic anhydride converts **1** to **5** in good yield. The results are summarized in Table I.

Although Pd/C can be used for the hydrogenation of 1,3,5-trinitrobenzene,[1] it is not effective for the hydrogenation of **1** itself. The ^1H NMR spectrum of **1** in Me_2SO indicates that **1** exists as **1a** rather than **1b** (see Experimental Section), which may explain why **1** is not hydrogenated over Pd/C. On the other hand, acyl derivatives of **1** appear to exist in the aromatic form, and Pd/C catalyzes the hydrogenation of **1** in the presence of acetic anhydride. Excess acetic anhydride (6 molar equiv/mol of trioxime) is necessary to obtain good yields of **5**.



1a **1b**

n-Butyl acetate is a good solvent for this reduction, whereas the more polar solvent acetic acid gives a low yield of **5**. The differences between the two solvents were revealed by following the reductions with TLC. In *n*-butyl acetate, the reduction proceeded slowly to give **4**–**6**; in acetic acid, hydrogen uptake occurred at the beginning of the reduction but gradually stopped, and TLC analysis showed the formation of **6**–**8** and only a small amount of **5**. All of these compounds were isolated, and their structures were assigned on the basis of their chemical and spectral properties. *n*-Butyl acetate is not a very good solvent for the reduction products, which precipitate on the catalyst and stop the hydrogenation; addition of a small amount of acetic acid to the initial reaction mixture gives better yields of **5**. The reaction sequence of eq 1 appears reasonable for the hydrogenation in *n*-butyl acetate. It appears that, in acetic acid, the hydroxy groups of the oxime are readily acetylated and that these acetoxy derivatives are not reduced. This surmise is supported by our observation that the triacetoxy derivative **8** is essentially unchanged by treatment with hydrogen and Pd/C in acetic acid at 80 °C.

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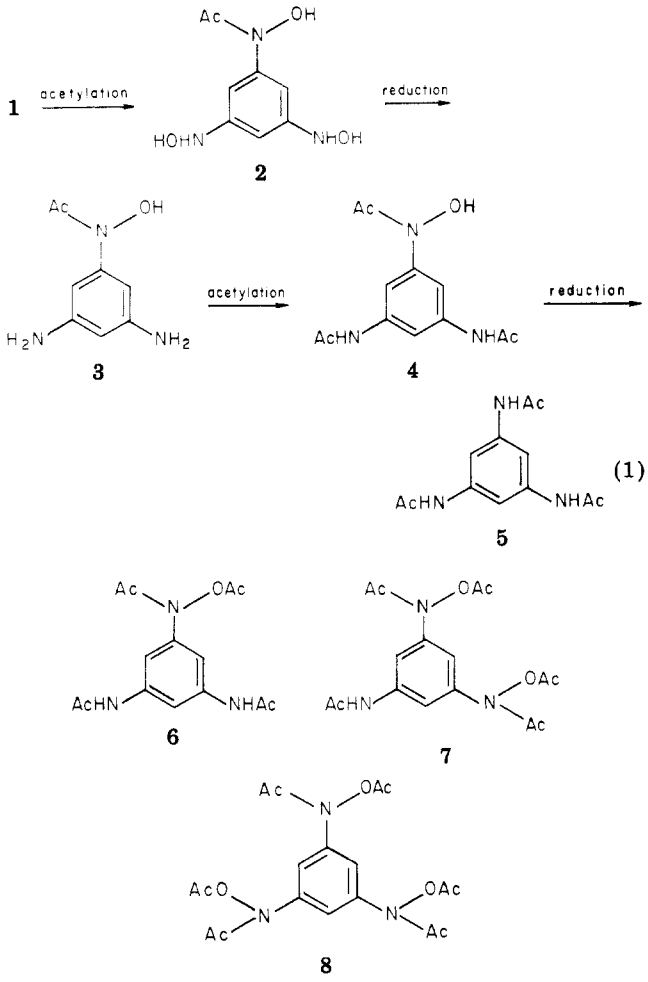

Hydrogenation of 1 with Raney Ni catalyst in *n*-butyl acetate solution proceeds rapidly. After filtration to remove the catalyst, treatment of the reaction mixture with acetic anhydride gives **5** in high yield.

Reduction of 1 with zinc and acetic acid also proceeds readily. Since 1,3,5-triaminobenzene is not stable in acetic acid, the reaction was carried out in the presence of acetic anhydride to convert the triaminobenzene into **5**, which was isolated in good yield.

Experimental Section

General Comments. Melting points were determined with a hot-stage microscope and are uncorrected. ^{1}H NMR spectra were obtained on deuteriodimethyl sulfoxide solution by using a JEOL FX-100 spectrometer. Elemental analyses were performed by Toyo Jozo Co. Phloroglucinol trioxime (1) was prepared from phloroglucinol and hydroxylamine according to the method of Baeyer:[3] ^{1}H NMR 3.04, 3.24, 3.50 (s, 6 H, CH_2), 10.71, 10.74, 10.81 (s, 3 H, OH). Palladium on carbon (5%) and Raney nickel (NDHT-90) were purchased from Kawaken Fine Chemical Co. TLC was carried out by using silica gel plates developed with ethyl acetate.

Reduction of Phloroglucinol Trioxime (1). (1) Palladium on Carbon. (a) In *n*-Butyl Acetate. To a mixture of 1.7 g (0.01 mol) of 1 and 5.6 mL (0.06 mol) of acetic anhydride in 50 mL of *n*-butyl acetate containing 0.5 mL of acetic acid was added 340 mg of 5% palladium on carbon. The mixture was stirred under hydrogen at 80 °C for 6 h, while 800 mL of hydrogen was absorbed. The catalyst and white precipitate were separated by filtration and extracted with ethanol under reflux. The ethanol extract was concentrated, and the residue was recrystallized from aqueous ethanol to yield 1.6 g (65%) of 1,3,5-tris(acetamido)benzene (**5**) which was identified by comparison with an authentic sample:[3] mp 342 °C; ^{1}H NMR δ 2.04 (s, 9 H, Ac), 7.61 (s, 3 H aryl), 9.88 (s, 3 H, NH).

Anal. Calcd for $C_{12}H_{15}N_3O_3$: C, 57.82; H, 6.07; N, 16.86. Found: C, 57.56; H, 6.16; N, 16.89.

From the mother liquid were isolated by crystallization 0.4 g (15%) of 1,3-diacetamido-5-(*N*-acetylhydroxyamino)benzene (**4**) and 0.5 g (16%) of 1,3-diacetamido-5-(*N*,*O*-diacetylhydroxyamino)benzene (**6**). For **4**: mp 132 °C (from aqueous EtOH); ^{1}H NMR δ 2.03 (s, 6 H, Ac), 2.18 (S, 3 H, Ac), 7.58 (d, J = 2 Hz, 2 H, aryl), 7.72 (t, J = 2 Hz, 1 H, aryl), 9.92 (s, 2 H, NH). Anal. Calcd for $C_{12}H_{15}N_3O_4 \cdot 2H_2O$: C, 47.84; H, 6.36; N, 13.95. Found: C, 47.83; H, 6.38; N, 13.97.

For **6**: mp 211 °C (from aqueous EtOH); ^{1}H NMR δ 2.05 (s, 9 H, Ac), 2.26 (s, 3 H, OAc), 7.44 (d, J = 2 Hz, 2 H, aryl), 7.86 (t, J = 2 Hz, 1 H, aryl), 10.04 (s, 2 H, NH). Anal. Calcd for $C_{14}H_{17}N_3O_5$: C, 54.72; H, 5.58; N, 13.67. Found: C, 54.52; H, 5.59; N, 13.84.

Compound **4** was acetylated with acetic anhydride and pyridine to give **6**, and **6** was deacetoxylated by hydrogenation with 5% palladium on carbon in ethanol to give **5**.

(b) In Acetic Acid. A mixture of 1.7 g (0.01 mol) of 1, 5.6 mL (0.06 mol) of acetic anhydride, and 340 mg of 5% palladium on carbon in 50 mL of acetic acid was stirred under hydrogen at 80 °C for 3 h. The catalyst was separated by filtration, and the filtrate was evaporated to dryness. The resulting residue was chromatographed on silica gel with ethyl acetate for elution to yield a small amount of **5**, 0.3 g (10%) of **6**, 0.9 g (25%) of 1,3-bis(*N*,*O*-diacetylhydroxyamino)-5-acetamidobenzene (**7**), and 0.6 g (15%) of 1,3,5-tris(*N*,*O*-diacetylhydroxyamino)benzene (**8**).

For **7**: mp 156 °C (from CCl_4); ^{1}H NMR δ 2.07 (s, 3 H, Ac), 2.10 (s, 6 H, Ac), 2.30 (s, 6 H, OAc), 7.34 (t, J = 2 Hz, 1 H, aryl), 7.69 (d, J = 2 Hz, 2 H, aryl), 10.20 (s, 1 H, NH). Anal. Calcd for $C_{16}H_{19}N_3O_7$: C, 52.60; H, 5.24; N, 11.50. Found: C, 52.64; H, 5.27; N, 11.94.

For **8**: mp 130 °C (from CCl_4); ^{1}H NMR δ 2.12 (s, 9 H, Ac), 2.32 (s, 9 H, OAc), 7.55 (s, 3 H, aryl). Anal. Calcd for $C_{18}H_{21}N_3O_9$: C, 51.07; H, 5.00; N, 9.93. Found: C, 50.69; H, 4.99; N, 9.70.

1,3,5-Tris(*N*,*O*-diacetylhydroxyamino)benzene (8). A mixture of 1.7 g (0.01 mol) of 1 and 5.6 mL (0.06 mol) of acetic anhydride in 20 mL of acetic acid containing a few drops of concentrated sulfuric acid was stirred at room temperature for 20 h. The solution was then evaporated to dryness, and the residue was chromatographed on silica gel with ethyl acetate for elution to yield 2.1 g (50%) of **8**.

(2) Raney Nickel. A mixture of 1.7 g (0.01 mol) of 1 and 5 g of Raney nickel in 50 mL of *n*-butyl acetate was stirred under hydrogen at 80 °C for 3 h, while 700 mL of hydrogen was absorbed. The catalyst was separated by filtration and washed with ethyl acetate. The filtrate was then concentrated to 50 mL. Colorless crystals (1.1 g) were formed and identified as 1,3,5-triaminobenzene by comparison with an authentic sample.[1] To the above concentrated solution was also added dropwise with stirring 3 mL of acetic anhydride. A white precipitate immediately formed and was separated by filtration and dried to yield 2.2 g (88%) of **5**.

(3) Zinc in Acetic Acid. To a mixture of 1.7 g (0.01 mol) of 1 and 5.6 mL (0.06 mol) of acetic anhydride in 50 mL of acetic acid was added with stirring 5 g of zinc dust. The mixture was stirred at room temperature of 0.5 h. Then another 5 g of zinc dust was added, and the mixture was heated at 80 °C for 1 h. An additional 5 g of zinc dust was added, and the mixture was stirred for another 2 h. Zinc was separated by filtration, and the filtrate was evaporated to dryness. The resulting residue was recrystallized from aqueous ethanol to yield 2.0 g (80%) of **5**.

Table I. Reduction of Phloroglucinol Trioxime [a]

reducing agent	solvent	% yield of 5
H_2, Pd/C	*n*-BuOAc, HOAc, Ac_2O	65
H_2, Pd/C	HOAc, Ac_2O	trace
H_2, Raney Ni	*n*-BuOAc	88 [b]
Zn	HOAc, Ac_2O	80

[a] The temperature was 80 °C in all cases. [b] Reaction mixture was treated with Ac_2O after the reduction.

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Registry No. 1a, 621-22-7; 4, 78870-34-5; 5, 26243-62-9; 6, 78870-35-6; 7, 78870-36-7; 8, 78870-37-8.

A Simple, Remarkably Efficient Route to High Purity, Crystalline 9-Borabicyclo[3.3.1]nonane (9-BBN) Dimer

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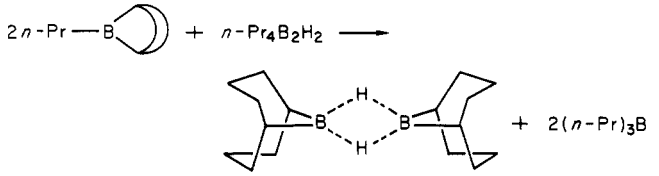
9-Borabicyclo[3.3.1]nonane (9-BBN) is a stable, crystalline dialkylborane, which, owing to its remarkable selectivity, has found wide application in organic synthesis.[1] We report a new, highly efficient preparation of crystalline 9-BBN dimer in high yield and purity from the cyclic hydroboration of 1,5-cyclooctadiene with borane–methyl sulfide complex, using 1,2-dimethoxyethane (monoglyme) as the reaction solvent. The product obtained under these conditions is resistant to decomposition in air and is indefinitely stable under a nitrogen atmosphere at room temperature. This development also makes possible the purification of 9-BBN from commercial and other sources to give a high purity, stable product.

First isolated and characterized by Köster,[2] 9-BBN dimer (1) was obtained from the thermal redistribution of *B*-*n*-propyl-9-BBN.



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However, since the preparation of the *B*-alkyl-9-BBN derivative was itself a two-step process,[3] a more attractive route to 9-BBN was found by Knights and Brown, involving the cyclic hydroboration of 1,5-cyclooctadiene with borane–tetrahydrofuran complex.[4]

A 70:30 mixture of the isomeric 9-borabicyclo[3.3.1]- and [4.2.1]nonanes were formed in the initial cyclic hydroboration step. However, simply heating the mixture at reflux temperature effected equilibration of the boranes to give 1 exclusively. This procedure gives a microcrystalline product of mp 142 °C in ca. 65% yield. Further purification of this material by vacuum sublimation increases the melting point to 152–155 °C.[5]

While this approach is a particularly convenient method for the preparation of 9-BBN, it suffers from several practical difficulties which diminish the yield and purity of the crystalline product actually obtained. For one, the choice of BH_3·THF as the reagent used for the initial hydroboration necessarily requires that THF be used as the reaction solvent. However, 9-BBN is significantly soluble in this medium, presumably due, at least in part, to the presence of an equilibrium concentration (ca. 14%) (see Table I) of a 9-BBN·THF complex (2).

$$\underset{1}{(\text{9-BBN})_2} \overset{\text{THF}}{\rightleftharpoons} \underset{2}{2\,\text{9-BBN·THF}}$$

Further, the microcrystalline product (1) obtained from THF solvent occasionally contains minor amounts of impurities which render the material pyrophoric.

Studies on the hydroboration of 1,5-cyclooctadiene using borane–methyl sulfide complex had revealed that this reagent could be used to prepare solutions of 9-BBN in solvents other than THF.[6] Of such solvents, the relatively low solubility of 9-BBN in diglyme[1] suggested that polyoxygenated ethers might provide an ideal reaction solvent to obtain the desired crystalline material.

The solubility of 9-BBN was measured in various solvents at 0 and 25 °C, and these results are summarized in Table II.

After investigating several solvent systems we found that monoglyme provided a superior reaction medium in that large crystals of 9-BBN dimer could be obtained in excellent yield (88%) and high purity (mp 153–155 °C). The high-purity crystalline 9-BBN dimer obtained from re-

Table I. Complexation of 9-BBN with Basic Solvents

base	% complex	^{11}B chemical shift[a] ($J_{^{11}B-H}$)
THF	14	13.9 (~90 Hz)
$S(CH_3)_2$	46	3.9 (107 Hz)
NC_5H_5[b]	100	-0.7 (88 Hz)

[a] Chemical shifts are reported in parts per million with BF_3·$O(CH_2CH_3)_2$ (δ = 0.00 ppm) as an external standard. Absorbances due to dimeric 9-BBN were observed at 28 ppm for the first two entries. The percent complexation was calculated from the relative peak areas from complexed vs. dimeric 9-BBN. [b] $CDCl_3$ was used as solvent in this case. Excess pyridine showed no measurable effect on the chemical shift of the boron resonance.

Table II. Molar Solubility of Dimeric 9-BBN in Representative Solvents[a]

solvent	temperature 0 °C	temperature 25 °C
monoglyme	0.01	0.07
diglyme	<0.01	0.04
1,4-dioxane	0.03[b]	0.07
1,3-dioxolane	<0.01	0.04[c]
diethyl ether	0.09	0.18
tetrahydrofuran	0.12	0.29
dichloromethane	0.11	0.28
chloroform	0.21	0.50
carbon tetrachloride	0.15	0.36
pentane	0.13	0.23
hexane	0.11	0.25
benzene	0.19[d]	0.36
cyclohexane	0.03[e]	0.08
toluene	0.14	0.33
dimethyl sulfide		0.60[f]

[a] Values determined by hydride analysis.[14] [b] 15 °C. [c] Some chemical change in 9-BBN was observed in this solvent. [d] 4.4 °C. [e] 7 °C. [f] Value taken from ref 1.

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