Table I. Computed Stabilization Energies of the Polyacenes

compound	DEPE[a]	REPE[a]
benzene	0.333	0.065
naphthalene	0.368	0.055
anthracene	0.380	0.047
tetracene	0.385	0.042
pentacene	0.388	0.038
infinite polyacene[b]	0.403	0.022

[a] In units of β. [b] Reference 7.

graphitene (0.020 β), mentioned by Haymet. For comparison, REPE = 0.053β for graphite. Thus the isolation[12] of **2** which has a considerably higher REPE than **1** does not have a strong bearing on the potential isolation of **1**. The computed REPE of **1** is higher than that of azulene (0.023 β); but in the benzenoid series, where there are usually many possibilities for rearrangement to more stable systems, an REPE of this size does not guarantee stability.[5]

Registry No. Footballene, 99685-96-8.

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A Unique Application of the Sulfide Reduction Useful for the Preparation of Isomerically Pure Aromatic Nitro Compounds and Anilines

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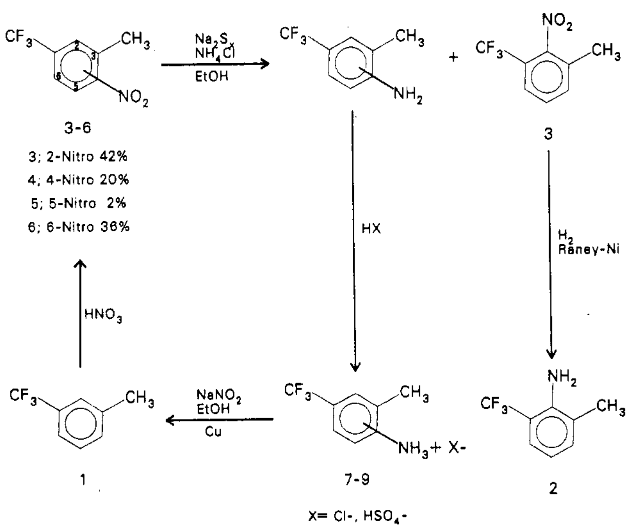
The preparation of isomerically pure substituted aromatic nitro compounds and anilines continues to be an important aspect of agricultural and pharmaceutical chemistry.[1] Since nitration, which is usually the most expeditious manner to prepare such chemicals, invariably gives mixtures of isomers that are often difficult to separate, a practical laboratory method to obtain pure isomers would be of general interest and utility. Recently, we encountered a need to prepare pure **2**. To achieve this, a chemical method was discovered whereby the separation could be effected through a simple laboratory procedure. Reported here is a unique application of a sulfide (Zinin) reduction of a mixture of nitration isomers useful to obtain both **3** and **2** isomerically pure.

The *m*-xylene derivative **1**, which could be obtained in good yield by a published method,[2] was nitrated to afford a complicated mixture of nitro compounds[3] (cf. Scheme I). Interestingly, the most hindered isomer, **3**, was the major product (42%). It is known, however, that nitration of *m*-toluic acid and *m*-tolualdehyde gives the analogous isomer as >50% of their product mixture.[4]

Separation of the mixture was effected by a unique application of the Zinin reduction.[5] While sulfide salts are known to reduce pure nitration isomers,[6] they are also sensitive to the steric environment of the nitro group.[5]

Scheme I



Thus, we expected to see some kinetic differentiation among the isomers **3-6**. This turned out to be true since we saw a clean conversion of isomers **4-6** to their respective anilines (**7-9**) without any observable alteration of **3** (cf. Scheme I). In fact, the anilines **7-9** were precipitated from dichloromethane by gaseous HCl in 88% yield while **3** was isolated in 95% yield.

The rate of reduction was pH sensitive and required that caustic be added to maintain pH >10.5. It was also important to keep the pH <12 to mitigate the loss of aniline products which were prone to decomposition in the presence of strong hydroxide. We found that the polysulfide reagents were milder and preferable to the monosulfide salts. Ultimately a buffered system was developed using sodium disulfide and ammonium chloride to lower the pH into the 11-12 range. Pure ammonium disulfide could not be used since its pH was <10.5. Other buffers and conditions were studied, and none showed any improvement over those given here. Eventually, this procedure was optimized so that the reduction could be run with a pH meter to monitor the caustic concentration. After complete reaction (GLC), the crude product was worked up with the anilines either being extracted into acid or the entire mixture being dissolved in dichloromethane and the anilines precipitated with HCl gas in 88% yield (Scheme I). Crude **3**, obtained in 95% yield (40% from **1**), was either crystallized or reduced directly to **2** with Raney Ni under H_2 atmosphere. The reduction to **2** proceeded in 95% yield (cf. Scheme I).

The overall process was made extremely efficient when anilines **7-9** as their H_2SO_4 salts were reductively deaminated to recover **1** in 83% yield (cf. Scheme I).

We investigated several other approaches to perform this unique method of separating the nitration isomers without success. Efforts to find a selective catalyst for hydrogenation failed while examination of the literature did not reveal any simple alternatives to the Zinin reduction.

Other examples were run to test the general nature of this reaction. In one example *m*-xylene was nitrated to get the usual 85:15 ratio of isomers. Reaction of this mixture with sodium sulfide proceeded at a much slower rate due to the lack of an additional electron-withdrawing group. However the 2-nitro isomer could be cleanly separated, albeit in a poor yield.

Experimental Section

All NMR spectra were recorded on a Varian EM-390 NMR spectrometer at 90 MHz. All chemical shifts are reported in parts

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per million (ppm) relative to tetramethylsilane (Me$_4$Si) as an internal standard for proton spectra and benzotrifluoride (BTF) as an external standard for fluorine spectra. Gas chromatography was performed with a Varian Model 3700 gas chromatograph and a 10-ft 10% OV-11 column. All solvents and reagents used were not purified prior to use, and melting points were uncorrected.

Nitration of 3-Methylbenzotrifluoride. At 0 °C 90% nitric acid (500 g, 7.2 mol) was stirred as 3-methylbenzotrifluoride (160 g, 1.0 mol) was added at a rate such that the reaction temperature never exceeded 5 °C. Upon complete addition the solution was stirred for 15 min, after which the reaction was poured cautiously over ice/water (2 kg). The layers were separated and the aqueous layer was washed with dichloromethane (1 × 500 mL). The organics were combined, dried (MgSO$_4$), filtered, and concentrated to 200 g of the crude nitration mixture (97%). Capillary GLC analysis showed a mixture of 42% 3-methyl-2-nitrobenzotrifluoride (**3**), 36% 3-methyl-6-nitrobenzotrifluoride (**6**), 20% 3-methyl-4-nitrobenzotrifluoride (**4**), and 2% 3-methyl-5-nitrobenzotrifluoride (**5**). Each component was compared to an authentic sample prepared via an unambiguous route.[7]

Disulfide Reduction of the Nitration Mixture. At 40 °C, Na$_2$S·9H$_2$O (84 g, 0.35 mole) was treated in 1:1 methanol/water (200 mL) with sulfur (13.8 g, 0.4 mol) in one portion followed by methanol (100 mL). Within 1 h all solids had dissolved, and ammonium chloride (4.7 g, 0.0875 mol) was added and stirred for 15 min. The temperature was brought to 75 °C in a separate reactor containing the nitration mixture (57.4 g, 0.28 mol) in 1:1 methanol/water (50 mL). The polysulfide reagent was added slowly over a 1-h period. After a brief exotherm the reaction slowed and 25% NaOH was added to maintain pH 11–12. After a total of 5 h the mixture was cooled, diluted with water (500 mL), and extracted with dichloromethane (3 × 100 mL). The organic layer was treated with gaseous HCl resulting in the precipitation of the hydrochlorides of **7**–**9**. Filtration recovered 29.5 g (88%) of the yellow anilinium salts. Concentration of the filtrate gave 24.8 g (95%) of a dark oil which crystallized on standing. Recrystallization from methanol or methylcyclohexane gave analytically pure **3**: ^{1}H NMR (CDCl$_3$) 2.2 (s, 3 H), 7.3 (s, 4 H); ^{19}F NMR (CDCl$_3$) +2.3; mp 32–33 °C; bp 48–49 °C at 0.1 mmHg.[7]

Reductive Deamination of 7, 8, and 9. The reduction was run as shown above with 17.7 g of the nitration mixture. The crude products, extracted into dichloromethane, were treated slowly with 50% sulfuric acid (10 mL) at 0 °C. The acid layer was estimated to have 50 mmol of anilinium hydrogen sulfate salt dissolved while the organic phase was concentrated to give 7.0 g of **3**. Thus this acidic solution was treated with the cautious addition of NaNO$_2$ (3.5 g, 52 mmol) in water (15 mL) at 0 °C. The reaction was vigorous and upon complete addition of nitrite this cold solution was added dropwise to ethanol (20 mL) and Cu–bronze (0.5 g) at reflux. The resulting solution was refluxed for 30 min, after which it was cooled, diluted with dichloromethane (100 mL) and washed with water (1 × 30 mL). The organic layer was dried (MgSO$_4$), filtered, and fractionally distilled to recover 6.6 g of **1** (83%).

Reduction of 3-Methyl-2-nitrobenzotrifluoride (3). A Parr hydrogenation apparatus was used to reduce **3** (5.2 g, 25 mmol) in ethanol (100 mL) with Raney Ni catalyst (1 g). Hydrogen was charged to 50 psi, and the apparatus was shaken for 24 h at room temperature. At the end of this period of time the catalyst was filtered and concentration of the solvent gave 4.2 g of aniline (**2**) (95%): ^{1}H NMR (CDCl$_3$) 2.1 (s, 3 H), 4.0 (bs, 2 H), 6.6–7.2 (m, 3 H); ^{19}F NMR (CDCl$_3$) −5.2; bp 64–66 °C at 5 mmHg.[7]

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Registry No. **1**, 401-79-6; **2**, 88301-98-8; **3**, 81-20-9; **4**, 67192-42-1; **5**, 96783-80-1; **6**, 87617-21-8; **7**, 23984-80-7; **8**, 103981-82-4; **9**, 103981-83-5.

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[7] These products were identical in all respect with those materials reported in ref 3.

Improved Synthesis of 1,4,5,8,9,12-Hexaazatriphenylene

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The synthesis and some properties of 1,4,5,8,9,12-hexaazatriphenylene (HAT, **3**) have recently been reported.[2] HAT is a stronger electron acceptor than 1,10-phenanthroline and forms mono-, di, and trichromium tetracarbonyl complexes. The previously reported synthesis is an involved 10-step procedure. Because we required multigram quantities of HAT, we needed a more practical preparation.

The approach we took is shown in Scheme I. Although 1,3,5-triamino-2,4,6-trinitrobenzene (TATB, **1**) has been reduced to the hexaamine with boiling phenylhydrazine[3] and more recently catalytic hydrogenation,[4] we explored reduction with sodium in liquid ammonia, which has previously been used for reduction of mononitroarenes.[5,6] Symmetric peralkyl derivatives of HAT have recently been synthesized by condensation of hexammine **2** with α-diketones; the method reported was not successful in producing HAT itself.[7]

A wide variety of standard methods for reduction of aromatic nitro groups were surveyed without success. The low stability of HAB was a contributing factor in these failures. A review of the literature showed that various mononitroarenes had been successfully reduced to amines by sodium in liquid ammonia in the presence of methanol.[5,6] In these cases typically 10 equiv of alcohol were used.

When we applied these procedures to the reduction of TATB, some HAB was produced but in low and variable yield. Instead of the transient blue color expected in a dissolving metal reduction, the reaction mixture was an intense purple color. A review of the earlier literature[4] indicated that this color was typical of the reaction of nitroarenes with sodium and liquid ammonia in the absence of hydrogen donors. We therefore examined the use of very high concentrations of the hydrogen donor in these reactions.

In our case the use of 42 equiv of methanol per nitro group gave reproducible yields of HAB in excess of 90%. Little or no purple color formation occurred; the usual transient blue color followed by a fading yellow color was observed. We made no attempt to determine the minimum amount of methanol required. It seems likely that protonation of the intermediate reduction products is in competition with other reaction routes such as coupling and that use of high concentrations of the hydrogen donor favor the desired reduction to an amine.

HAT of good purity was produced in over 80% yield by simply adding freshly prepared HAB to 40% aqueous glyoxal. The crude HAT was purified to give material of analytical quality by simple column chromatography. Overall this procedure gives analytical quality HAT in

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