

A SAFE AND CONVENIENT NEW PROCEDURE FOR REDUCING AROMATIC
COMPOUNDS TO BIRCH-TYPE PRODUCTS

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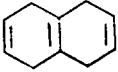
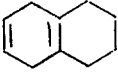
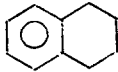
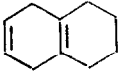
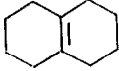
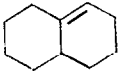
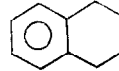
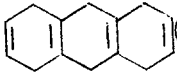
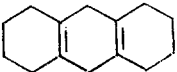
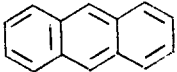
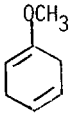
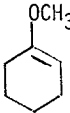

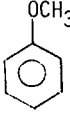
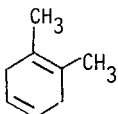
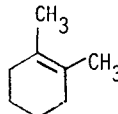
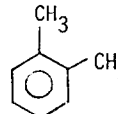
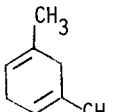
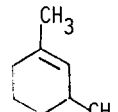
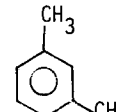
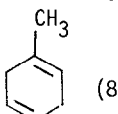
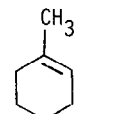
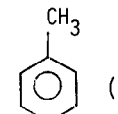
Abstract: Aromatic compounds can be reduced by a calcium-amine-*t*-butyl alcohol system to products which are identical to those obtained by a Birch reduction of the same substrates.

Recently we¹ disclosed that aromatic hydrocarbons are reduced by calcium in certain amine solvents to cyclic monoenes. We now wish to report that by varying reaction conditions, the calcium-amine system can be used to reduce aromatic compounds to products which previously were obtained by Birch-type reductions (Table 1).

The calcium-amine-alcohol procedure has certain advantages over the sodium² or lithium³ reductions carried out in liquid ammonia or amines⁴ in the presence of a proton source like alcohols. First of all, calcium is much safer to handle than sodium or lithium and hence the calcium procedure is much more amenable to large scale reductions (see reduction of *p*-xylene below). Likewise the amine solvents are relatively high boiling and therefore much easier to manipulate than liquid ammonia. This is the first general procedure ever developed whereby calcium can be used to reduce aromatic ring systems to Birch-type products. The detailed procedures which follow for the preparation of 1,4,5,8,9,10-hexahydroanthracene and 1,4-dimethyl-1,4-cyclohexadiene are typical of the methods employed for virtually all the reductions reported in Table 1.

An oven dried, three-neck 500 mL round bottom flask was fitted with a Hershberg stirrer,⁵ gas inlet tube and an air-cooled Allihn condenser. The system was flushed with argon whereupon calcium shot⁶ (4.0 g; 0.1 g at), white sand (24 g), anthracene (4.45 g; 0.025 mol) and *t*-butyl alcohol⁷ (3.7 g; 0.05 mol) were added all at once. All exits of the flask were protected with mercury-mineral oil bubblers. A mixture of freshly distilled *n*-butylamine (38 mL), dry⁸ ethylenediamine (38 mL) and THF (90 mL) were added next and the flask was immersed in an ice-bath. Stirring was started, and, after 25 min the remaining *t*-butyl alcohol (11.1 g; 0.15 mol) was added dropwise over a 25 min period. After 24 h only small pieces of calcium remained in the gray, viscous mixture. Technical diethyl ether (100 mL) was added followed by cautious hydrolysis with an aqueous solution of NH₄Cl (27 g in 100 mL of H₂O). A rather vigorous reaction⁹ usually accompanied the hydrolysis step. The remainder of the work-up was quite similar to that described elsewhere.^{1a} A yellow solid (4.6 g; 100%) was obtained which was a

Table 1. Reduction of Certain Aromatic Compounds by a Calcium-Amine-*t*-Butyl Alcohol Procedure.

Substrate	Product Composition (%) ^{c,d,e}	References
1. Naphthalene ^a	 (81);  (16);  (2)	f
2. Tetralin ^a	 (89);  (6);  (2);  (1) (2)	
3. Anthracene ^a	 (76);  (6);  (2)	g
4. Anisole ^b	 (86);  (3);  (7);  (4) (2)	
5. <i>o</i> -Xylene ^b	 (75);  (6);  (13)	h
6. <i>m</i> -Xylene ^b	 (90);  (5);  (2)	h
7. <i>p</i> -Xylene ^b	 (88);  (11);  (1)	h

a) The overall yield was 90-95%. b) The overall yield was 70-80%. The lower yields were due to the inevitable loss of volatile products during work-up. c) In those cases where the percentages listed do not total 100%, the remainder of the material was of unknown composition. d) All analytical work was carried out on a Varian Model 3700 capillary gas chromatograph. When samples were collected for spectroscopic studies, an Aerograph 200 instrument was used. e) The identity of each product was established either by a ¹H NMR spectra (Perkin Elmer R-32 spectrometer operating at 90 MHz in 5 mm tubes) or by ¹³C NMR (Varian XL-200 spectrometer operating at 50.3 mHz in 10 mm tubes). f) Hüchel W.; Schlee, H. *Chem. Ber.* 1955, 88, 346. g) Mejer, S.; Proycki, J.; Jablonski, L. *Rocz. Chem.* 1977, 51, 1755. h) Krapcho, A. P.; Bothnerby-By, A. A. *J. Am. Chem. Soc.* 1959, 81, 3658.

mixture (GLPC analysis; SE-30 capillary column; 60 m x 0.25 mm) of 1,4,5,8,9,10-hexahydroanthracene (76%), 1,2,3,4,5,6,7,8,9,10-decahydroanthracene (6%) and 2% anthracene. Recrystallization of the mixture from petroleum ether (30-60°C) yielded 2.9 g (63%) of the desired product as a white solid¹⁰ melting at 146-147°C; lit.¹¹ 147-148°C.

As described above for anthracene, calcium (12.0 g; 0.3 g at), white sand (24 g), *p*-xylene (21.2 g; 0.2 mol) and *t*-butyl alcohol (4.9 g; 0.066 mol) were placed in a 1 L three-neck flask which had been previously oven-dried and flushed with argon. *n*-Butylamine (150 mL) and ethylenediamine (150 mL) were added. After this mixture was allowed to stir for 40 min, the remaining *t*-butyl alcohol (39.5 g; 0.534 mol) was added over a 40 min period. The mixture was stirred¹² for 24 h, during which time a gray solid developed. After the usual workup, distillation yielded 13.6 g (63%) of material boiling at 140-2°C. Analysis by GLPC (SE-30 capillary column; 60 m x 0.25 mm) indicated the presence of 1,4-dimethyl-1,4-cyclohexadiene of 92% purity. The structure was confirmed¹³ by ¹H and ¹³C NMR.

There are several points in connection with reductions by calcium that are worthy of further comment. First of all, we now recommend the use of a Hershberg stirrer along with sand for all calcium reductions. This combination effectively removes the insoluble coatings which form and which adhere rather tightly to the calcium surface usually necessitating the use of a large excess of the metal. We have found that all coating problems encountered in this and previous research^{1a} involving calcium are completely obviated by the Hershberg stirrer-sand technique. The abrasive action which this combination provides, effectively removes coatings from calcium surfaces.¹⁴ Secondly, we have found that reductions depicted in Table 1 are much more selective when carried out at 0°C rather than at ambient temperatures. Pure ethylenediamine freezes at about 9°C and hence the presence of a second amine (*n*-butylamine¹⁵ in the case of anthracene) provides a solvent mixture which remains fluid at 0°C. A wide variety of other substances can be used to prevent the freezing out of the ethylenediamine, but these will be reported later.¹⁶ There is an additional advantage to the "anti-freeze" additive in that the ratio of the ethylenediamine and the other additives can be varied to maximize the solubility of the substrate. In the reduction of anthracene, a mixture of *n*-butylamine and THF along with the ethylenediamine seemed to afford the best combination for solubility. In all cases the ethylenediamine was an essential ingredient of the solvent mixture. Only in pure methylamine did calcium reductions proceed at all and the product distribution was very complex.

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5. (a) Hershberg, E. B. *Ind. Eng. Chem., Anal. Ed.* 1936, 8, 313. (b) Pinkney, P. S. *Org. Synth. Coll. Vol. II*, 1943, 116. The Hershberg stirrer we used in this work had only one glass ring and one strand of Chromel-20 gauge wire as pictured on p. 117 of ref. 5b.
6. Ca shot (99.5%) purchased from Alfa Products was used.
7. Very likely other alcohols will work or may even be superior to *t*-butyl alcohol. We are in the process of screening other alcohols.
8. We have found the drying of ethylenediamine to be a very critical point. Drying over sodium as we did in our earlier work (ref. 1; see also Reggel, L.; Friedel, R. A.; Wender, I. *J. Org. Chem.* 1957, 22, 891) is not the best procedure. When it is dried this way, there may be induction periods varying from a matter of minutes to hours before some of the reductions will start. We have traced this problem to the presence of moisture or HCO_3^- . We now recommend that the ethylenediamine (Aldrich, 99+%) be stirred over fresh NaOH pellets for at least 24 h and then refluxed for 3 h over CaO before a final distillation. Using ethylenediamine dried this way virtually eliminates the induction periods.
9. The use of an ice bath is recommended here.
10. ^1H NMR (CDCl_3 , Me_4Si) δ 2.39 (s, 4 H), 2.52 (s, 8 H), 5.7 (s, 4 H). ^{13}C NMR (CDCl_3 , Me_4Si) δ 30.5, 35.92, 123.4, 124.5.
11. Runge, V. J. *J. Prakt. Chem.* 1966, 31, 280.
12. Although the mixture was allowed to stir for 24 h, the reaction was virtually complete at the end of 7 h. This was also true for *m*-xylene (Table 1, entry 6) where the reduction was virtually complete after 11 h.
13. ^1H NMR (CDCl_3 , Me_4Si) δ 1.65 (s, 6 H), 2.54 (s, 4 H), 5.4 (broad s, 2 H). ^{13}C NMR (CDCl_3 , Me_4Si) δ 23.1, 73.0, 118.6, 131.2.
14. To demonstrate this point, we carried out an experiment in which 0.25 g at (10 g) of calcium was stirred in 75 mL of ethylenediamine for 19 h using an ordinary (paddle-type) laboratory stirrer. At this time approximately 50% of the calcium was used up and a gray precipitate had formed in the solution. The latter was very likely the result of amide formation resulting from a direct reaction between the calcium and ethylenediamine. To this slurry, 0.025 mol (2.7 g) of *p*-xylene was added and the stirring was continued for 4.5 h. An aliquot was withdrawn and was shown by GLPC to contain 3% of 1,4-dimethylcyclohexene. After an additional 20 h of stirring, only 9% of the latter compound had formed. At this point the mechanical stirrer was replaced by a Hershberg stirrer and white sand was added. After an additional 24 h of stirring, a 62% yield of 1,4-dimethylcyclohexene was obtained.
15. We have ascertained that when *n*-butylamine is used alone, no reduction occurs. Thus, when 0.025 mol of *p*-xylene was stirred with 0.125 g at of calcium in 75 mL of *n*-butylamine for 4 days, 88% of the *p*-xylene was recovered unchanged.
16. Unpublished studies by Miss Angela Rappa. The usual solvent system consists of a mixture of ethylenediamine and *n*-butylamine. This mixture was used for all cases in Table 1 except for anthracene where THF was also added.

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