# Rhodium Sulfide Catalyzed Reductive Alkylation of 1,5-Naphthalenediamine

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The utility of metal sulfide hydrogenation catalysts for the reductive alkylation of primary aryl amines with aliphatic ketones has recently been disclosed.[1-5] Rhodium sulfide appears to be the most active of these catalysts for reductive alkylations. We now describe its use in the preparation of several new N,N′-dialkyl-1,5-naphthalenediamines.

Reactions of 1,5-naphthalenediamine with acetone, cyclohexanone, methyl ethyl ketone, and methyl isobutyl ketone went smoothly and resulted in high yields of the corresponding N,N′-dialkyl-1,5-naphthalenediamines. A preformed 5% rhodium sulfide on carbon catalyst was used in each case. In addition, a catalyst prepared *in situ* from 5% rhodium on carbon and hydrogen sulfide was used in one experiment with acetone.

## Experimental Section

The 1,5-naphthalenediamine was purchased from Aldrich Chemical Co., Inc. The ketones used were reagent grade chemicals. The rhodium on carbon and rhodium sulfide on carbon catalysts were obtained from Engelhard Industries, Inc.

Yields of crude residue products were 96% or higher in each case. Yields of pure products were not determined but are estimated to be in excess of 90%.

A detailed description of one experiment is given to illustrate the procedure.

To a 600-ml stainless steel Magne–Dash autoclave were added 31.6 g (0.20 mole) of 1,5-naphthalenediamine, 200 ml (*ca.* 2.7 moles) of acetone, and 2.5 g of 5% rhodium on carbon. The autoclave was sealed, purged with nitrogen and then with hydrogen. Hydrogen sulfide was added to a pressure of 50 psig, followed by the addition of hydrogen to a pressure of 1300 psig. The reaction mixture was heated with agitation at 140° and 1200–1400 psig for 3 hr. The autoclave was cooled and depressurized and the reaction product removed. The reaction mixture was filtered to remove catalyst; the solvent was removed by distillation. The solid residue, crude N,N′-diisopropyl-1,5-naphthalenediamine, weighed 47 g and melted at 114–126°. The melting point was 130–132° after one recrystallization from acetone–water. Recrystallization from a mixture of benzene and hexane, followed by a recrystallization from hexane, gave white crystals, mp 134–135°. *Anal.* Calcd for $C_{16}H_{22}N_2$: C, 79.29; H, 9.15; N, 11.56. Found: C, 80.07; H, 9.26; N, 11.31. The dihydrochloride, prepared by reaction with concentrated hydrochloric acid in 95% ethanol, melted at 284° dec. *Anal.* Calcd for $C_{16}H_{24}N_2Cl_2$: Cl, 22.49. Found: Cl, 21.82.

The following experiments were run in a 2-l. stainless steel Magne–Dash autoclave with 94.9 g (0.60 mole) of 1,5-naphthalenediamine, 700 ml of ketone, and 5.0 g of 5% rhodium sulfide on carbon without added hydrogen sulfide.

**N,N′-Diisopropyl-1,5-naphthalenediamine.**—The reaction mixture containing *ca.* 9.5 moles of acetone was heated at 130–135° and 900–1100 psig for 2 hr. There was obtained 144 g of a crude residue of N,N′-diisopropyl-1,5-naphthalenediamine melting at 115–121° (mostly 118–121°).

**N,N′-Dicyclohexyl-1,5-naphthalenediamine.**—The reaction mixture containing *ca.* 6.7 moles of cyclohexanone was heated at 125–130° and 900–1100 psig for 3.5 hr. There was obtained 197 g of a crude residue melting at 159–194° (mostly 189–194°). Several recrystallizations from a mixture of benzene and 2-propanol gave a white powder, mp 195–196°. *Anal.* Calcd for $C_{22}H_{30}N_2$: C, 81.93; H, 9.38; N, 8.69. Found: C, 82.77; H, 9.54; N, 8.38.

**N,N′-Di-*sec*-butyl-1,5-naphthalenediamine.**—The reaction mixture containing *ca.* 7.8 moles of methyl ethyl ketone was heated at 120° and 900–1100 psig for 2.3 hr. There was obtained 161 g of a crude residue melting at 78–99° (mostly 95–99°). Several recrystallizations from hexane gave a pale yellow powder, mp 114–114.5°. *Anal.* Calcd for $C_{18}H_{26}N_2$: C, 79.95; H, 9.69; N, 10.36. Found: C, 80.06; H, 9.65; N, 10.93.

**N,N′-Di-1,3-dimethylbutyl-1,5-naphthalenediamine.**—The reaction mixture containing *ca.* 5.6 moles of methyl isobutyl ketone was heated at 130° and 800–1200 psig for 9 hr. There was obtained 188 g of a semisolid, crude residue. Several recrystallizations from methanol gave white needles, mp 104.5–105°. *Anal.* Calcd for $C_{22}H_{34}N_2$: C, 80.92; H, 10.50; N, 8.58. Found: C, 81.42; H, 10.73; N, 8.80.

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[4] F. S. Dovell and H. Greenfield, *J. Am. Chem. Soc.*, **87**, 2767 (1965).

[5] H. Greenfield and F. S. Dovell, paper presented at 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965; Division of Petroleum Chemistry Preprint B-121.

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# Nuclear Magnetic Resonance Spectra of Some Polyphenyl-2,3-diazanaphthalenes and -2,3-diazaanthracenes

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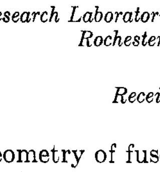
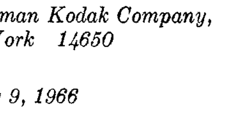
The geometry of fused-ring aromatic systems is such that substituents in the *peri* positions are forced into close proximity, giving rise to nonbonded interactions over unusually short distances. For example, phenyl substituents in the *peri* positions of naphthalene and anthracene are forced to rotate out of normal conjugation with the polycyclic ring,[1] one result being that protons in substituents *peri* to such phenyl rings are located in the diamagnetic shielding zone of the pendant phenyl ring,[2] and should resonate at higher field intensity than usual for the particular substituent. The nmr absorption of the pendant phenyl groups in the spectrum of 1,8-diphenylnaphthalene, for example, falls 0.5–0.6 ppm to higher field than the pendant phenyls of naphthalenes with nonadjacent phenyls.[3]

The preparation of some polyphenyl-substituted 2,3-diazanaphthalenes (**1** and **2**) and 2,3-diazaanthracenes (**3–5**) provides examples of *peri*–*peri* interaction in a



**1**, R = H
**2**, R = Ph



**3**, $R_1 = CH_3$; $R_2 = H$
**4**, $R_1 = Ph$; $R_2 = H$
**5**, $R_1 = R_2 = Ph$

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