Metal–Amine Reactions.[1] The Effect of Continuous Sodium Dispersions during Reaction with Naphthalene

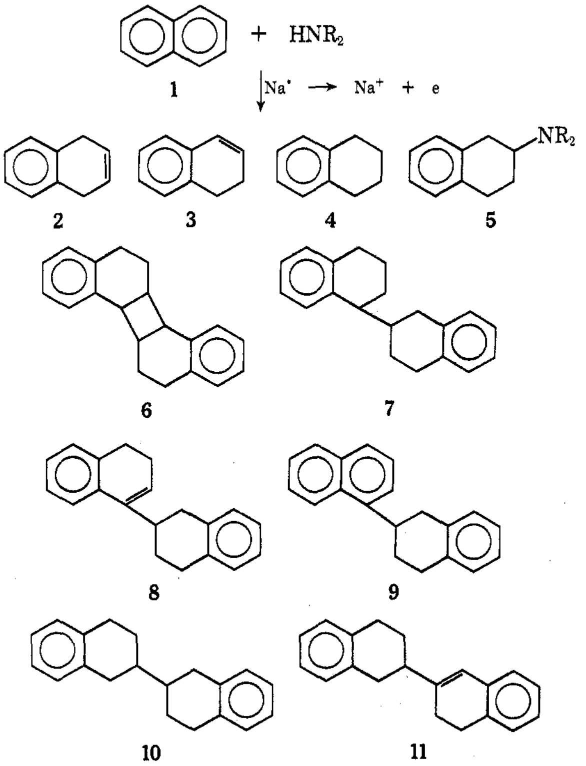
L. E. HARRIS,[2a] D. V. HERTZLER,[2b] O. C. DERMER, AND E. J. EISENBRAUN*

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74074

Received February 23, 1972

We previously demonstrated that, in addition to reduction products, naphthalene and alkylnaphthalenes in the presence of sodium and secondary amines give reductive amination (*e.g.*, **5**) and/or reductive dimerization products (*e.g.*, **6**, **7**, **8**, **9**, **10**, and **11**) of Scheme I.[1]

SCHEME I



We were also able to show that, with proper selection of an unhindered amine (cyclic secondary amine), reductive amination becomes the predominant route or, conversely, with a hindered secondary amine (*e.g.*, dipropylamine) or primary diamines (*e.g.*, ethylenediamine), reductive amination diminishes and reductive dimerization predominates.[1b] In some cases, formation of specific dimerized hydrocarbons is markedly selective.[1a,d]

With the techniques that had been developed in the earlier work, some reactions were sluggish and the yields were disappointingly low. We were dependent upon the use of dispersed sodium and a paddle stirrer or magnetic stirrer for agitation.

In either case, initially the reaction proceeded satisfactorily. However, the dispersed sodium soon agglomerated to a few shiny balls of metal. To overcome this difficulty, we developed a stir–shredding device which simultaneously stirs and disperses sodium, thus continuously exposing new surface and re-forming fine particles.[3] The development of this apparatus removed the need for using predispersed sodium, and it became possible to carry out reactions with sodium and an amine by periodically adding small pieces or pellets of sodium directly to the reaction mixture. The continuous shredding action provides fresh surface, increases solubility, and hence increases the possibility of reaction. The overall result is a reduction in reaction time and an increased yield of reductive amination product. The data from several selected reactions are compiled in Table I.

Our principal interest in this study was to increase the yield of reductive amination product. A 3-hr reaction period (*vs.* 12-hr previously used) was adequate to cause an increase in yield in all cases and even more than double the yield of reductive amination product in some cases.

It should be noted that extending the reaction period from 3 to 6 hr for *N*-methylpiperazine caused the yield of reductive amination product to drop from 95 to 57%. Similarly, the reaction with pyrrolidine after 20 hr showed 64% yield of reductive amination as compared to 78% after 3 hr. We attribute this lowering of yield to a reversal of reductive amination product formation.[1b] Hence, the best yields of reductive amination are to be expected in a rapid reaction using an unhindered amine. Accordingly, hindered secondary amines should not, and indeed do not, give high yields of reductive amination product. However, it is of interest that, through the use of the stir–shredding apparatus, hindered amines (2-methylpiperidine, 2,6-dimethylpiperidine, dipropylamine, and diisopropylamine) show small increases in reductive amination product, as compared to the yields reported in the earlier work.[1b]

Experimental Section[4]

General Reaction Conditions.—All reductions were carried out in a similar manner using the previously described stir–

---

[1] (a) L. E. Harris and E. J. Eisenbraun, *J. Org. Chem.*, **37**, 336 (1972); (b) E. J. Eisenbraun, R. C. Bansal, D. V. Hertzler, W. P. Duncan, P. W. K. Flanagan, and M. C. Hamming, *ibid.*, **35**, 1265 (1970); (c) R. C. Bansal, E. J. Eisenbraun, and P. W. Flanagan, *J. Amer. Chem. Soc.*, **88**, 1837 (1966); (d) E. J. Eisenbraun, D. V. Hertzler, R. C. Bansal, P. W. K. Flanagan, and M. C. Hamming, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **13** (3), 55 (1968).

[2] (a) Continential Oil Company Graduate Research Fellow, 1970–1971; (b) National Science Foundation Science Faculty Fellow, Grant 68098, 1968–1969.

[3] E. J. Eisenbraun and H. Hall, *Chem. Ind. London*, 1158 (1971).

[4] (a) The solvent amines, obtained from Union Carbide Co. and Aldrich Chemical Co., were dried by stirring (24 hr) with KOH and distilling from fresh KOH. The high-purity naphthalene was a gift from Sun Oil Co. The sodium (Matheson Coleman and Bell Co.) was reagent grade, 0.1–0.25 in. spheres, and was washed with sulfuric acid treated and redistilled petroleum ether, bp 60–68°, before use. (b) The glc analyses of the dimeric hydrocarbons and the reductive amination products were obtained on a Hewlett-Packard 5750 glc apparatus fitted with thermal conductivity and hydrogen flame detectors using helium as the carrier gas. For the reductive amination products, a 0.25 in. × 10 ft column of 5% polyethylenimine on base-washed firebrick (80–120 mesh) at 190 to 230° was used. The dimer hydrocarbon mixtures were analyzed on a 0.25 in. × 11 ft column of 6% UC W-98 methyl–vinyl silicone rubber on acid-washed and DMCS-treated Chromosorb G (80–100 mesh) at 260°. (c) The nmr spectra (CCl$_4$) were obtained with Varian HR-60 and HA-100 instruments (TMS standard) and mass spectra were obtained with a Consolidated Electrodynamics Corp. Model 21-103C mass spectrometer. (d) The glc analyses of the steam-volatile hydrocarbons were obtained on a Beckman GC-2A glc apparatus fitted with a thermal conductivity detector using a 0.25 in. × 10 ft column of 25% Carbowax 20M on Chromosorb W (30–60 mesh) at 190°.

TABLE I

METAL–AMINE REACTIONS

Amine	Reaction time,[a] hr	Distilled reductive amination products, %[b,c]	Naphthalene recovered, %	Yield[b] of hydrocarbon, %				Glc ratio of C_{20} dimers						
				2	**3**	**4**	Nonvolatile	**6**	**7**	**8**	**9**	**10**	**11**	Unknown
				Using the Stir–Shredding Device										
N-Methylpiperazine	3	95		<1	1	<1	1		17	36	35	12		
	6	57	1	1		1	1		25	39	14	22		
Piperidine	3	79	<1	2	2	<1	2	1	68	12	6	13		
Pyrrolidine	3	78	<1	<1	<1	4	8	2				98		
	20	64				6	13					100		
N-Methylbutylamine	3	78	<1	2	5	2	9		64	21	6			9
Diethylamine	3	13	2	2	13	13	56		42	39	10			9
Ethylenediamine	3	*d*	5	13	3	2	42	27	25	1		2	20	25
2-Methylpiperidine	3	13[e]	33	9	15	2	50		41	38	21			
2,6-Dimethylpiperidine	3	*f*	25		17	5	63		71	19	10			
Dipropylamine	23	12[g]	49			6	62		11	16	73			
Diisopropylamine	27		61			4	65		28		69		3	
				Using Predispersed Sodium and Magnetic Stirring[h]										
N-Methylpiperazine	12	64		6	<1		5	1		17		71		11
Piperidine	12	46		4	<1		11	2				94		4
Pyrrolidine	12	35		20			36	2				98		
2-Methylpiperidine	12	5		42			36							
2,6-Dimethylpiperidine	12			5	4		85							

[a] At room temperature. [b] Yield based on consumed naphthalene. [c] Nonvolatile reductive amination products remained at still bottoms and were not measured. [d] Consisted of several products (1.6 g). [e] Consisted of two major products, 79% of the expected one and 17% of one with the same glc retention time as the amination product from piperidine. [f] Two products (1.3 g) which showed molecular ion *m/e* 229 in their mass spectra and not 243 as expected for the amination product. [g] Consisted of several unidentified products. [h] Ref 1b.

shredding device.[3] The equipment was dried before assembling and a flow of dry lamp-grade nitrogen was employed to flush the system for 10 min before any reactants were added. A thermocouple, inserted through one of the openings at the top and immersed in the solution, was used to monitor the temperature. A rubber cooling tube[5] wrapped around the outer wall of the reaction flask was used to maintain the reaction mixture at room temperature.

The amine and **1** were introduced through a port at the top of the flask and stirred until the solution was complete.[4a] Sodium was then added slowly over a period of 1–2 hr from a 125-ml erlenmeyer flask attached by Gooch tubing to one of the addition ports.[4a] The sodium addition was slow enough to allow the metal spheres of each portion to be shredded into small pieces before more was added. A yellow-orange color usually developed in less than 10 min with most amine solvents. This color darkened to red and then to a red-brown color within 1–2 min and the solution became opaque. The color of the reaction mixture usually remained dark red-brown to brown against a muddy-appearing background.

Reduction of Naphthalene (1) with Sodium and *N*-Methylbutylamine.—To 12.8 g (0.1 mol) of **1** and 250 ml of *N*-methylbutylamine[4a] (bp 88–90°) contained in the reaction flask was added 9.2 g (0.4 g-atom) of sodium over a period of 1.5 hr. A yellow color developed on the metal surface immediately and the solution turned red-orange in *ca.* 2 min. This color darkened to red-brown in 30 sec and after 8 min the solution had gradually darkened to an opaque brown. This appearance remained until the reaction mixture was decanted from the unreacted sodium at the end of 3 hr and was poured cautiously over 400 ml of crushed ice. The resulting orange mixture was extracted with 500 ml of ether in three portions, and the ether layer was washed once with water and then twice with 10% aqueous HCl. The ether layer, which retained the hydrocarbons, was then washed with water until neutral. The acidic extracts and water washings were combined, made basic with NaOH, and extracted with ether. The amine-carrying ether layer was washed with water, dried (Na_2SO_4), and concentrated to yield 17.9 g of amines. Distillation at reduced pressure yielded 16.7 g (78%) of *N*-butyl-*N*-methyl-1,2,3,4-tetrahydro-2-naphthylamine, which appeared pure by glc analysis:[4b] bp 86° (0.2 mm); mass spectrum[6] (70 eV) *m/e* (rel intensity) 217 (25), 174 (100), 131 (71), 70 (20), 44 (35), 42 (33); nmr (CCl_4) four aromatic protons at δ 6.92 (singlet) and 19 aliphatic protons at 0.3–3.1 (several overlapping multiplets), with a singlet at 2.21.[4c]

Anal. Calcd for $C_{15}H_{23}N$: C, 82.89; H, 10.67; N, 6.45. Found: C, 82.90; H, 10.61; N, 6.78.

The ether layer containing the hydrocarbons was concentrated and steam distilled. Both pot residues and distillate were extracted with ether and dried (Na_2SO_4). Distillation of the ether from the extract of the distillate yielded 1.3 g of steam-volatile hydrocarbons. These were shown by glc analysis to be a mixture of **1**:**2**:**3**:**4** (8:22:50:28).[4d]

The ether extract of the pot residue was concentrated (rotary evaporator) to yield 1.2 g of a dark viscous oil. This was shown by glc analysis to be a mixture of dimers **7**, **8**, and **9**, in which dimer **7** is the major one.[4b]

The reaction procedure and product analysis techniques given above are identical to those used for the other reaction products shown in the first part of Table I. The reductive amination products were shown by instrumental methods to be identical in structure with authentic samples of the expected amines.

Registry No.—Naphthalene, 91-20-3; *N*-methylbutylamine, 110-68-9; sodium, 7440-23-5; *N*-butyl-*N*-methyl-1,2,3,4-tetrahydro-2-naphthylamine, 35046-15-2.

Acknowledgments.—We thank the American Petroleum Institute for partial support.

---

[5] The tubing is made of thermal conducting material with a hemispherical cross section which allows close fit to the flask surface.

[6] We thank Mr. M. C. Hamming, Continential Oil Co., for this determination.