

Metal-Amine Reactions.¹ The Reductive Amination of Aromatic Hydrocarbons²

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Received September 22, 1969

The reductive amination of polynuclear aromatic hydrocarbons provides a new synthesis of novel secondary and tertiary amines. The conditions affecting this reaction of aromatic hydrocarbons with alkali metals and amines were studied. Reductive amination takes place concurrently with, and at times in preference to, metal-amine reduction when an aromatic hydrocarbon is treated with sodium and a secondary or primary amine. This side reaction to the Birch-type reduction takes place readily with naphthalene and alkylated naphthalenes and generally at the β position of the less substituted ring, provided that there is no alkyl group at either vicinal position. Steric effects in both the aromatic hydrocarbon and in the amine influence the competition of reductive amination and Birch-type reduction.

The reduction of naphthalene to 1,2,3,4-tetrahydronaphthalene (1) by sodium in liquid ammonia was first studied in 1914.⁵ Later it was shown that four atoms of sodium were involved, though a large excess was present.⁶ In 1939, naphthalene was shown to react with two atomic proportions of sodium in liquid ammonia at -75 to -65° to form a red complex which, on decomposition with methanol, gave 1,4-dihydronaphthalene (2).^{7a} The complex was found to be stable at low temperatures but ammonolyzed above -50° to form 2, which was isomerized to 1,2-dihydronaphthalene (3). The latter isomer then reduced at this temperature to 1. It was therefore concluded that the reduction of naphthalene to 3 is a stepwise process, involving successive formation of a disodium adduct, protonolysis of the adduct to 2 and sodium amide, base-induced rearrangement of 2 to 3, and, finally, reduction to 1. Similar results were obtained with calcium.^{7a} It was inferred that the organometallic intermediates in these reactions are salts, and that the reduction is initiated by the addition of electrons to the naphthalene nucleus to form a radical anion and dianion. Other contributions to our understanding of dissolving metal reactions have been made^{7b-f} and general discussions are available.^{7g-i}

Birch, in the early 1940's, greatly extended Wooster's earlier observations,^{6,8} and, as a result, the Birch re-

duction has been applied extensively in synthetic organic chemistry.^{7e} The Birch reduction of polynuclear aromatic hydrocarbons and other aromatic systems has been thoroughly explored and reviewed.⁹ Birch routinely included alcohols in his reaction mixtures. These were considered to be the source of protons for the reduction of aromatic systems.

Other authors have modified the original procedure utilized by Birch. Significant contributions regarding the relative merits of lithium and sodium resulted from the work of Wilds and Nelson¹⁰ and, subsequently, from that of Dryden and coworkers^{11a} and Harvey.^{11b} The use of calcium hexamine in the selective reduction of aromatic hydrocarbons has been reported.^{11c} Benkeser and coworkers pioneered the use of low molecular weight amines such as methylamine, ethylamine, and propylamine instead of liquid ammonia.¹² More extensive reduction results when these amines are used, since there is an increase in solubility of organic molecules and the reaction temperature may be higher. Reggel and coworkers showed that lithium in ethylenediamine appears to be the most powerful metal-amine system and can reduce aromatic hydrocarbons to saturated hydrocarbons.^{13a-c} Slaugh and Raley^{13d} reported reduction of benzene and alkyl-substituted benzenes with sodium-ammonia at 60 – 130° . Reduction of aromatic hydrocarbons has also been achieved by electrolysis in the presence of lithium chloride using a low molecular weight amine or ethylenediamine^{14a} or hexamethylphosphoramide^{14b} solvent.

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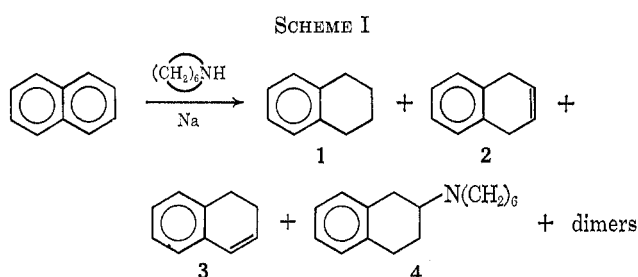
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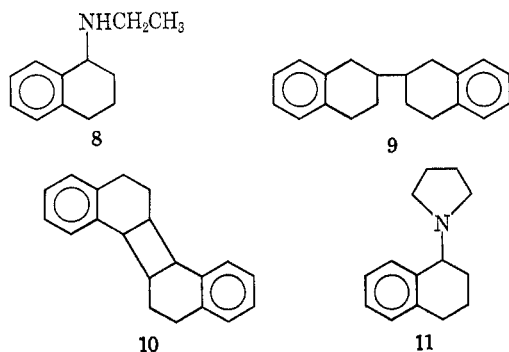
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Results and Discussion

We previously demonstrated^{1,2} that amines and sodium may be used in the reduction of naphthalene and alkylated naphthalenes to dihydronaphthalenes and tetrahydronaphthalenes. However, in some cases, the low yields of reduced hydrocarbons pointed to the formation of side reaction products. These were identified as hydrocarbon dimers^{2b,15} and secondary or tertiary amines, of which N-(1,2,3,4-tetrahydro-2-naphthyl)hexamethylenimine (**4**) is typical. The hydrocarbon reduction products accompanying **4** are shown in Scheme I. In the case of naphthalene, **1** is the dominant volatile hydrocarbon product, and with certain amines, the presence of **2** can be detected^{2b} in the early stages of the reaction. The tertiary amine **4** results from amination of **3**.¹



Various primary and secondary amines were used to test the generality of the reductive amination reaction. The results are summarized in Table I. Reductive amination products and hydrocarbon dimers (reductive dimerization) exceed the Birch-type reduction products when primary amines are used. For example, cyclohexylamine and *n*-hexylamine gave 33 and 28% yields of N-cyclohexyl-1,2,3,4-tetrahydro-2-naphthylamine (**5**) and N-*n*-hexyl-1,2,3,4-tetrahydro-2-naphthylamine (**6**), respectively, whereas N-ethyl-1,2,3,4-tetrahydro-2-naphthylamine (**7**) and N-ethyl-1,2,3,4-tetrahydro-1-naphthylamine (**8**) were obtained in 17% combined crude yield and the conventional Birch-type reduction products were essentially absent. The hydrocarbon dimers are a complex mixture, of which 1,2,3,4,1',2',3',4'-octahydro-2,2'-binaphthyl (**9**)¹⁶ and 5,6,6a,6b,11,12,12a,12b-octahydrodibenzo[*a,g*]biphenylene (**10**) generally predominate.^{2b}

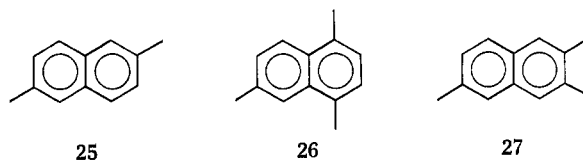


The dimer **9** has been reported to form in the reaction of naphthalene with sodium¹⁶ and ethylamine or with either sodium^{17a} or magnesium^{17b} and ammonia.

The formation of a carbon-nitrogen bond during reductive amination generally takes place at the β position of the naphthalene nucleus. The observed major exceptions occur with ethylamine and pyrrolidine (Table I), which gave **8** and 1-pyrrolidino-1,2,3,4-tetrahydronaphthalene (**11**), respectively. In both cases, these are the minor products.

The yield of reductive amination product appears to be very susceptible to steric effects in the amine moiety. For example, 2-methylpyrrolidine and 2-methylpiperidine afforded small amounts (*ca.* 1–5%) of reductive amination products, whereas 2,5-dimethylpyrrolidine and 2,6-dimethylpiperidine failed to give more than trace amounts of such products. However, all of these amines cause reduction and reductive dimerization of naphthalene, as shown in Table I.

Several alkyl-substituted naphthalenes were subjected to reductive amination with sodium and hexamethylenimine. The results may be found in Table II. It is of interest that reductive amination for these examples takes place in the less alkyl-substituted ring of the naphthalene nucleus and at the 2 position. If the ring is substituted by alkyl groups in both rings, reductive amination may not take place.^{1,2} For example, 2,6-dimethylnaphthalene (**25**), 1,4,6-trimethylnaphthalene (**26**), and 2,3,6-trimethylnaphthalene (**27**) failed to give reductive amination products; however, extensive Birch-type reduction or reductive dimerization of the individual hydrocarbons took place.



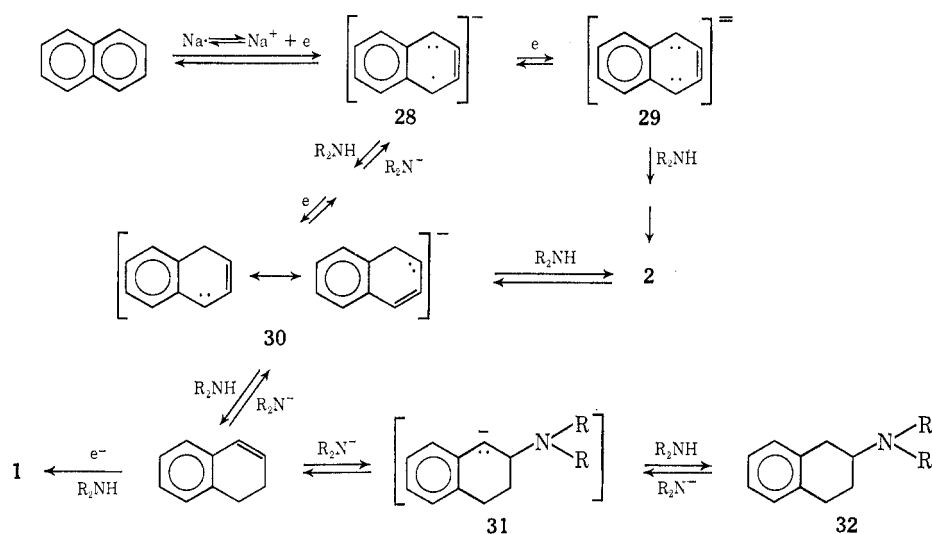
A definite assignment for the position of attachment of nitrogen for the reductive amination products from 1-methylnaphthalene, 2-methylnaphthalene, and 2-*t*-butylnaphthalene in Table II could not be made, since, for example, the nmr data did not permit distinction between **19a** and **19b**.

Consideration of the foregoing data and the probable mechanism^{7a} for formation of **1–3** strongly suggests the overall sequence in Scheme II. This rationalization explains the formation of 1,2,3,4-tetrahydronaphthalenes as well as reductive amination products from 1,2-dihydronaphthalenes. We suggest that, for reduction and presumably for reductive amination, the necessary protons come from the amine solvent and not from the water used to quench the reaction. We also suggest that the amination step takes place by nucleophilic addition of the anion of hexamethylenimine to the conjugated double bond of **3** and subsequent abstraction of a proton from hexamethylenimine by anion **31**, as shown in Scheme II. It seems less likely that addition to **2** takes place, since **2** is readily isomerized to **3**. Under the same conditions, cyclohexene and cyclooctene gave no evidence of reaction.

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SCHEME II


 TABLE I
 REDUCTIVE AMINATION OF NAPHTHALENE AT ROOM TEMPERATURE

Amine	Compd	Reductive amination products		Hydrocarbons ^a		
		Structure	% ^a	1	3	Dimers ^b
Cyclohexylamine	5		33	2	2	43
<i>n</i> -Hexylamine	6		28	0.3	0.8 ^c	47
Ethylamine ^d	7		17 ^e	...	1	80
Ethylenimine	12		<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>
Pyrrolidine	13		35 ^g	20	...	36
Piperidine	14		46	4	0.7	11
Hexamethylenimine	4		28	8	0.4	35
Morpholine	15		33	32	...	8
2,6-Dimethylmorpholine	16		52	7	7	12
<i>N</i> -Methylpiperazine	17		64	6	0.8	5
Dipropylamine	18		6	4	9	55
2-Methylpyrrolidine			5	23	...	30
2,5-Dimethylpyrrolidine			...	25	...	36
2-Methylpiperidine			5	42	...	36
2,6-Dimethylpiperidine			...	5	4	85

^a Yield based on consumed naphthalene. ^b Containing several dimers, of which 9 and 10 are major constituents. ^c This fraction contained ca. 25% 2. ^d At 15°. ^e Nmr analysis showed this product to be a mixture of 7 and 8 (16:1). ^f The extreme sensitivity of 12 to acid does not allow the usual isolation procedure, and only sufficient quantities of 12 for identification and analysis were isolated. The hydrocarbons were not investigated in this case. ^g Gas chromatography analysis showed this product to be a mixture of 11 and 13 (1:11).

SCHEME III

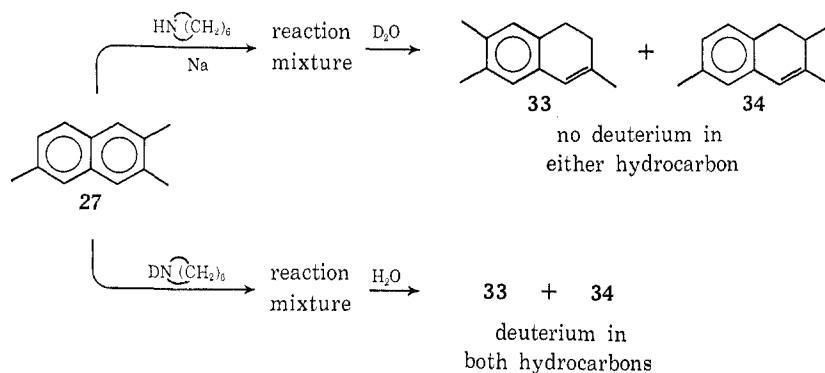


TABLE II

REDUCTIVE AMINATION OF ALKYLATED NAPHTHALENES WITH SODIUM AND HEXAMETHYLENIMINE AT 25°

Starting material	Yield of reductive amination product, ^a %	Structure of reductive amination products	Yield of hydrocarbon products, %	
			Steam-volatile ^b	Non-volatile ^b
1-Methylnaphthalene	17	and/or	37	21
2-Methylnaphthalene	43	and/or	24	15
2- <i>t</i> -Butylnaphthalene	43	and/or	15	7
1,4-Dimethylnaphthalene	51		17	8
2,3-Dimethylnaphthalene	69		11	7
1,4,5-Trimethylnaphthalene	25		37	8

^a Yield calculations based on consumed aromatic hydrocarbon. ^b The compositions of these hydrocarbon products remain under study.

Evidence to support Scheme II was obtained by subjecting 27, as shown in Scheme III, to conventional sodium and hexamethylenimine reaction conditions and subsequent hydrolysis of the reaction products with deuterium oxide to yield 33 and 34, which were shown by nmr and mass spectrometric studies to be completely free of deuterium. However, when N-deuteriohexamethylenimine was substituted for hexamethylenimine in the reaction and hydrolysis was effected with water, substantial deuterium incorporation was observed in 33 and 34. These studies gave 33 and 34 in a 5:1 ratio, which is in agreement with the data shown in Table II. The nmr studies showed that there was no positional selectivity in deuterium incorporation in 33 and 34. However, a preference for deuterium exchange at benzylic positions was observed for recovered 27.

That addition of amine anion to a conjugated olefin is reversible in the reductive amination reaction was

demonstrated by the competitive study shown in Scheme IV. The formation of hydrocarbons 1 and 3 and the mixture of amines 11 and 13 was confirmed through instrumental studies and conclusively establishes that reductive amination is indeed a reversible process.

SCHEME IV

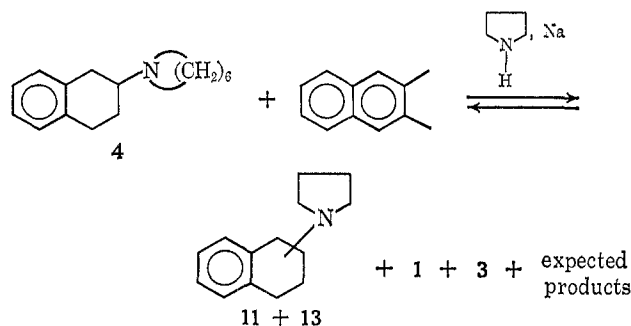
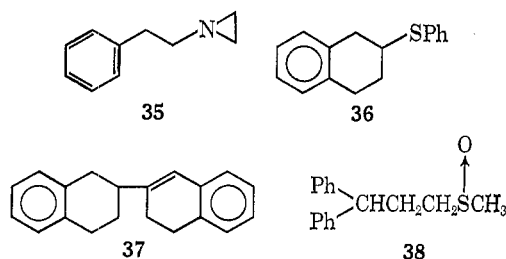


TABLE III
AMINATION OF 2 AND 3

Hydrocarbon	Amine	Source of base	Yield of 4, %	Yield of hydrocarbons, ^a %		
				1	3	Dimers
2	$\text{HN}(\text{CH}_2)_6$	Na	66	24	6	4
3	$\text{HN}(\text{CH}_2)_6$	Na	58	30	7	5
3	$\text{HN}(\text{CH}_2)_6$	<i>n</i> -BuLi	64	...	35	1

^a Yields determined by glpc analysis.

The addition of the anion derived from the reaction of *n*-butyllithium with hexamethylenimine to 2 and 3 (Table III) also substantiates Scheme II and is of interest because it takes place in a nonreducing system. Further, the addition of primary and secondary amines, in the presence of sodium to conjugated olefins is known.¹⁸ For example, styrene stirred with sodium and ethylenimine at 45° gives an 89% yield of 35.^{18a} Other experiments designed to test nucleophilic addition to 3 showed that 36 could be formed from the anion derived from the reaction of *n*-butyllithium and thiophenol but that sodium hydride in dimethyl sulfoxide caused the formation¹⁵ of the dimer 37 rather than the adduct comparable to 38 obtained from 1,1-diphenylethylene.¹⁹ The formation of dimer 37 may also be caused by heating 2 with potassium *t*-butoxide in DMSO²⁰ or by heating 2 or 3 with KOH in DMSO. The latter gives a mixture of dimers containing varying proportions of 9, 10, and 37.



Experimental Section²¹

The amines used in this work were purchased from the usual sources except for gift samples^{22a,b} and 2-methylpyrrolidine, which was prepared from 5-methyl-2-pyrrolidone by LiAlH_4 reduction. All amines were distilled from potassium hydroxide before use. The dispersed sodium was prepared by stirring freshly cut sodium pieces in hot xylene.

Structural Assignments.—The structures of the reductive amination products were assigned from nmr data summarized in

(18) (a) H. Bestian, *Justus Liebigs Ann. Chem.*, **566**, 210 (1950). (b) A. P. Stuart and C. E. Scott, U. S. Patent 3,118,938 (1964); *Chem. Abstr.*, **60**, 9167 (1964).

(19) C. Walling and L. Bolyky, *J. Org. Chem.*, **29**, 2699 (1964).

(20) Private communication from M. Baum. We acknowledge his prior preparation of 37, which proved to be identical with 37, from our reactions.

(21) Nmr spectra were obtained with a Varian HR-60 spectrometer. Peak positions are reported in terms of parts per million downfield from internal TMS standard in CCl_4 solvent. Mass spectra were obtained with a Consolidated Electrodynamics Corp. Model 21-103 C mass spectrometer. Glpc analyses for the hydrocarbons were obtained with a Hewlett-Packard Model 5750 gas chromatography apparatus fitted with thermal conductivity and hydrogen-flame detectors using helium as a carrier gas. The financial assistance from the Research Foundation, Oklahoma State University, PHS Grant 5-505-FR077-04, which made this instrument available is gratefully acknowledged. Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn.

(22) (a) We are grateful to the Union Carbide Co. for supplying amines used in the preparation of 6 and 15-18. (b) The ethylenimine used to prepare 12 was supplied by Dow Chemical Co. (c) We thank the Sun Oil Co. for the high-purity naphthalene used in these studies.

Table IV and observation of the molecular ion peak in the individual mass spectrum (Table V). Acceptable elemental analyses (C, H, and N) were obtained for each amine and are presented in Table VI.²¹

Reductive Amination of Naphthalenes.—All reductive amination reactions were carried out under a nitrogen atmosphere in a 300-ml, three-necked flask equipped with air condenser and magnetic stirrer. The reductive amination with ethylamine was carried out at 15° under a Dry Ice condenser, but in all other cases the reactions were carried out at room temperature.

Reductive Amination of Naphthalene with Sodium and Hexamethylenimine.—To 6.4 g (0.05 mol) of naphthalene^{22b} and 4.6 g (0.2 g-atom) of dispersed sodium contained in the reaction flask was added 100 ml of hexamethylenimine. A red color usually developed within 20 min. The mixture was stirred at 25° for 12 hr, and unreacted sodium which had agglomerated was removed. The reaction mixture was poured cautiously onto ice water and the red color disappeared. The product mixture was acidified with 10% aqueous hydrochloric acid. After the hydrocarbons had been removed by extraction with ether, the aqueous layer was made alkaline with dilute sodium hydroxide, and surplus hexamethylenimine was removed by steam distillation. The residue from steam distillation was extracted with ether. Drying (Na_2SO_4) gave 6.2 g (55% yield) of crude N-(1,2,3,4-tetrahydro-2-naphthyl)perhydroazepine (4); distillation gave a colorless oil (28% yield), bp 134–136° (0.8 mm).

The ether extract containing hydrocarbons was concentrated and then steam distilled to separate the volatile hydrocarbons from the C_{20} dimers. Extraction of the volatile fraction with ether, drying (MgSO_4), and concentrating afforded 0.55 g (8.4%) of a 20:1 (1 to 3) mixture. The ratio was determined by glpc on a Carbowax 20M column. Extraction of the residue of hydrocarbons from the steam distillation gave 2.3 g (35%) of a mixture of crude dimer hydrocarbon products, including 9 and 10. A similar procedure was used for the reductive amination of naphthalene with other amines.

Isolation and Identification of 1,2,3,4,1',2',3',4'-Octahydro-2,2'-binaphthyl (9) and 5,6,6a,6b,11,12,12a,12b-Octahydrodibenzo[a,g]biphenylene (10).—Dimer 9, mp 80–83°, crystallized from an ether extract of the previously described steam distillation as white crystals and was recrystallized: mp 84–85°; nmr (CCl_4) δ 6.99 (s, 8, ArH), 2.73 (q, 8, ArCH), and 1.65 (m, 6, CH_2); mass spectrum (70 eV) *m/e* (rel intensity) 262 (42), 131 (100), 130 (39), 129 (32), 104 (40), and 91 (29).

Dimer 10 crystallized from an ether solution of the nonvolatile hydrocarbon residue in the reaction of naphthalene with ethylenediamine. It was purified by crystallization from ether-petroleum ether as colorless crystals: mp 179–180°; nmr (CCl_4) δ 6.99 (s, 8, ArH), 2.76–3.46 (m, 6, ArCH), and 1.20–2.07 (m, 6, CH_2); mass spectrum (70 eV) *m/e* (rel intensity) 260 (41), 131 (38), 130 (40), 129 (100), 128 (63), and 115 (21).

Reductive Amination of Naphthalene with Sodium and Ethylenimine.—To 6.4 g (0.05 mol) of naphthalene and 4.6 g (0.2 g-atom) of dispersed sodium contained in the reaction flask, 100 ml of ethylenimine was added. After the mixture had been stirred at 25° for 12 hr, unreacted sodium was removed and the surplus ethylenimine was distilled under vacuum (water aspirator). The residue in the flask was diluted with water and shaken with ether. The ether extract was washed with water, dried over anhydrous sodium sulfate, and filtered. Distillation of ether gave 7.0 g of dark oil. Gas chromatographic analysis of this oil on a 10 ft \times 0.375 in. column of base-washed Chromosorb W coated with 25% Carbowax 20M showed 28% tertiary amine 12. Since 12 is very sensitive to acid, it was purified directly from the mixture by preparative gas chromatography using the above column.

Reduction of 2,3,6-Trimethylnaphthalene (27) with Sodium

TABLE IV
NMR DATA FOR REDUCTIVE AMINATION PRODUCTS

Compd	Aromatic protons absorption, δ ppm	Other proton absorptions, δ (ppm)
4	6.93 (4 H, s)	1.60 (8 H, s), ^a 1.14–2.25 (2 H, m), ^b 2.74 (9 H, m) ^c
5	6.89 (4 H, s)	0.61 (1 H, NH, s), 1.25–1.85 (12 H, m), ^b 2.71 (6 H, m) ^c
6	6.94 (4 H, s)	0.75 (1 H, NH, s), 0.88 (3 H, methyl, s), 1.31 (8 H, s), ^a 1.92 (2 H, m), ^b 2.70 (7 H, m) ^c
7 and 8	6.96 (4 H, s)	0.96 (1 H, NH, s), 1.08 (3 H, methyl, t), 1.72 (2 H, m), ^b 2.76 (7 H, m), ^c 3.82 (0.06 H, m) ^d
12	6.97 (4 H, s)	0.95 (2 H, t), ^e 1.20 (1 H, m), ^f 1.60–2.50 (2 H, m), ^g 1.56 (2 H, t), ^h 2.72 (4 H, benzylic, t)
11 and 13	6.92 (4 H, s)	1.67 (4 H, s), ^a 1.31–2.23 (2 H, m), ^b 2.61 (9 H, m), ^c 3.68 (0.43 H, m) ⁱ
14	6.91 (4 H, s)	1.47 (6 H, s), ^a 1.50–2.20 (2 H, m), ^b 2.46–2.69 (9 H, m) ^c
15	6.91 (4 H, s)	1.66 (2 H, m), ^b 2.55 (9 H, m), ^c 3.54 (4 H, q) ^j
16	6.93 (4 H, s)	1.15 (6 H, 2 methyl, d), 1.80–2.90 (11 H, m), ^{b,c} 3.25–4.00 (2 H, m) ^j
17	6.95 (4 H, s)	1.65 (2 H, m), ^b 2.20 (3 H, methyl, s), 2.26–2.90 (13 H, m) ^c
18	6.94 (4 H, s)	0.90 (6 H, methyl, t), 1.52 (4 H, m), ^a 1.90 (2 H, m), ^f 2.50 (4 H, t), ^h 2.77 (5 H, q) ^j
19a or 19b	6.81 (3 H, s)	1.22–1.93 (2 H, m), ^f 1.59 (8 H, s), ^a 2.13 (3 H, methyl, d), 2.68 (9 H, m) ^c
20a or 20b	6.76 (3 H, s)	1.26–1.89 (2 H, m), ^f 1.58 (8 H, s), ^a 2.21 (3 H, methyl, s), 2.69 (9 H, s) ^c
21a or 21b	6.95 (3 H, s)	1.28 (9 H, methyl, s), 1.59 (8 H, s), ^a 1.95 (2 H, m), ^f 2.72 (9 H, m) ^c
22	6.71 (2 H, s)	1.63 (10 H, s), ^a 2.14 (6 H, methyl, s), 2.66 (9 H, m) ^c
23	6.96 (2 H, s)	1.32–1.91 (2 H, m), ^b 1.58 (8 H, m), ^a 2.11 (6 H, methyl, s), 2.64 (9 H, m) ^c
24	6.72 (2 H, s)	1.11 and 1.23 (3 H, methyl, d, $J = 7$ cps), 1.60 (8 H, s), ^a 1.80–2.49 (2 H, m), ^b 2.14 and 2.23 (6 H, methyl), 2.68–3.30 (8 H, m) ^c

^a Methylene protons not adjacent to nitrogen. ^b Methylene protons not adjacent to nitrogen or aromatic ring. ^c Methylene protons adjacent to nitrogen or aromatic ring. ^d Protons adjacent to aromatic ring and nitrogen indicating 6% 8. ^e Methylene protons on one side of aziridine ring. ^f Methylene proton at C₃. ^g One methylene proton at C₂ and one at C₃. ^h Methylene protons on other side of aziridine ring. ⁱ Protons adjacent to aromatic ring and nitrogen indicating 43% 11. ^j Protons adjacent to oxygen. ^k Methylene protons adjacent to nitrogen. ^l Protons at C₁, C₂, and C₄.

and N-Deuteriohexamethylenimine.—A mixture of 3.29 g (0.02 mol) of 26, 3.0 g (0.13 g-atom) of sodium, and 100 ml of N-deuteriohexamethylenimine (65% D) was stirred at room temperature under a nitrogen atmosphere for 50 hr. The amine solution was decanted from the unreacted sodium and poured over crushed ice. The aqueous mixture was acidified with concentrated HCl and extracted twice with ether. The ether layer was washed twice with water and dried over anhydrous sodium sulfate, and the ether was distilled, leaving 2.8 g of oil. Unreacted starting material and compounds 33 and 34 were isolated by preparative gas chromatography. Mass spectrometric analysis of 33 showed the following incorporation (d_n , %) of deuterium: d_4 , 1; d_5 , 3; d_6 , 6; d_7 , 10; d_8 , 15; d_9 , 17; d_{10} , 17; d_{11} , 14; d_{12} , 9; d_{13} , 4; d_{14} , 2. The nmr spectrum did not show any selective deuterium incorporation. The mass spectrum of 34 showed the following incorporation (d_n , %) of deuterium: d_4 , 13; d_5 , 20; d_6 , 23; d_7 , 20; d_8 , 13; d_9 , 7; d_{10} , 2. The mass spectrum of recovered 27 showed the following incorporation (d_n , %) of deuterium: d_4 , 13; d_5 , 20; d_6 , 23; d_7 , 20; d_8 , 13; d_9 , 7; d_{10} , 2. The nmr spectrum showed the benzylic to aromatic proton ratio to be 6.2:5 compared with 9:5 for nondeuterated 27.

Exchange of Amino Groups in a Reductive Amination Product.—A mixture of 0.643 g (4.12×10^{-3} mol) of 2,3-dimethylnaphthalene, 1 g (4.12×10^{-3} mol) of 4, 0.379 g (1.65×10^{-2} g-atom) of sodium, and 16 ml of pyrrolidine were stirred under a nitrogen atmosphere for 12 hr. The amine and hydrocarbon products were separated by the procedure given for the reductive amination of naphthalene with sodium and hexamethylenimine. Gas chromatographic analysis of the volatile hydrocarbon mixture showed the presence of 1 and 3. Mass spectrometric analysis of the amine mixture which was not volatile to steam showed parent ions at m/e 229 and 201. This latter parent ion corresponds to the molecular weight of 11 or 13, which can arise only from an exchange of pyrrolidine for the hexamethylenimine group of 4.

An Attempted Reaction of Cyclooctene with Sodium and Hexa-

methylenimine.—A mixture of 5.5 g (0.05 mol) of cyclooctene, 4.6 g (0.2 g-atom) of sodium sand, and 150 ml of N-methylpiperazine was stirred at room temperature under a nitrogen atmosphere for 5 hr. No color developed and heat was not evolved from the reaction mixture. The reaction mixture was decanted from the sodium sand onto 400 ml of crushed ice. The aqueous reaction mixture was extracted with ether and the ether layer was extracted with excess 10% HCl. The ether layer was then dried (Na₂SO₄) and gas chromatographed. Only one peak, identical in retention time with that of cyclooctene, in addition to ether was observed. Under these conditions, cyclooctene would have been detected. A similar experiment with cyclohexene failed to produce any cyclohexane.

Reductive Amination of 1,2-Dihydronaphthalene (3) with Sodium and Hexamethylenimine.—A mixture of 5 g (0.04 mol) of 3, 3.5 g (0.15 g-atom) of sodium, and 150 ml of hexamethylenimine was stirred vigorously at room temperature for 20 hr under a continuous flow of nitrogen. The amine and hydrocarbon products were separated as previously described for the preparation of 4. The crude, gold-colored product (5.5 g) was distilled to give 5.1 g (58%) of 4, bp 137° (8 mm). The volatile hydrocarbon fraction was shown by glpc analysis to be a 4:1 mixture of 1 and 3. A trace of C₂₀ hydrocarbon dimers was isolated.

A duplicate run using 2 instead of 3 gave 4 in 66% yield and a 4:1 mixture of volatile hydrocarbons 1 and 3.

Reaction of 1,2-Dihydronaphthalene (3) and Hexamethylenimine by Means of *n*-Butyllithium.—To a 300-ml, three-necked flask equipped with condenser, stirrer, nitrogen inlet tube, and an addition funnel were added 100 ml of hexamethylenimine. A solution of 8% *n*-butyllithium–hexane (60 ml)²³ was added under nitrogen over a period of 15 min. The temperature of the reaction flask was maintained at 25° by external cooling. A solution

(23) The concentration of *n*-butyllithium was determined by hydrolysis of an aliquot and titration with standard hydrochloric acid.

TABLE V
 MASS SPECTRAL DATA OF REDUCTIVE AMINATION PRODUCTS

Compd	Molecular ion peak (intensity as % of Z)	Peaks by relative intensities fragmentation, m/e	Compd	Molecular ion peak (intensity as % of Z)	Peaks by relative intensities fragmentation, m/e
4	229 (4.5)	229, 124, 41, 225, 227, 128 ^a 230, 229, 228, 227, 226, 225 ^b	17	230 (3.4)	43, 58, 42, 70, 130, 230 ^a 231, 230, 229, 228, 186, 172 ^b
5	229 (6.0)	186, 130, 131, 229, 41, 56 ^a 230, 229, 187, 186, 158, 146 ^b	18	231 (1.7)	202, 131, 198, 27, 43, 41 ^a 231, 229, 227, 203, 202, 200 ^b
6	231 (3.3)	160, 131, 30, 130, 156, 231 ^a 232, 231, 230, 229, 227, 161 ^b	19a and/or 19b	243 (4.8)	243, 239, 41, 124, 129, 144 ^a 244, 243, 242, 241, 240, 239 ^b
7 and 8	175 (6.7)	175, 56, 130, 28, 131, 104 ^a 176, 175, 174, 173, 172, 171 ^b	20a and/or 20b	243 ^d (3.9)	239, 243, 41, 124, 241, 129 ^a 244, 243, 242, 241, 240, 239 ^b
11 and 13	201 (4.1)	28, 27, 96, 199, 201, 197 ^a 202, 201, 200, 199, 198, 197 ^b	21a and/or 21b	285 (3.0)	281, 266, 41, 285, 57, 124 ^a 286, 285, 284, 283, 282, 281 ^b
12	173 ^c (2.7)	130, 129, 115, 104, 28, 128 ^a 173, 172, 158, 147, 146, 145 ^b	22	257 (4.2)	253, 257, 158, 159, 41, 143 ^a 258, 257, 256, 255, 254, 253 ^b
14	215 (5.6)	110, 215, 211, 84, 213, 41 ^a 216, 215, 214, 213, 212, 211 ^b	23	257 (1.8)	98, 28, 253, 41, 255, 30 ^a 257, 256, 255, 254, 253, 252 ^b
15	217 (9.5)	217, 130, 112, 28, 131, 129 ^a 218, 217, 216, 215, 172, 159 ^b	24	271 (3.9)	28, 256, 271, 41, 157, 172 ^a 272, 271, 270, 269, 267, 257 ^b
16	245 (8.7)	245, 130, 131, 42, 129, 41 ^a 246, 245, 244, 243, 172, 160 ^b			

^a Six strongest peaks. ^b Last six peaks with intensities greater than 0.5% of total ion yield. ^c A 0.5% C₁₃H₁₇N impurity was detected. ^d Sample as the hydrochloride when admitted to mass spectrometer.

 TABLE VI
 ANALYTICAL DATA OF REDUCTIVE AMINATION PRODUCTS

Reductive amination products	Formula	Calcd, %			Found, %			Bp, °C (mm)
		C	H	N	C	H	N	
4	C ₁₆ H ₂₃ N	83.78	10.11	6.11	83.56	10.23	6.14	134-136 (0.8)
5	C ₁₆ H ₂₃ N	83.78	10.11	6.11	83.76	10.25	6.08	129-131 (0.8)
6	C ₁₆ H ₂₃ N	83.05	10.89	6.05	83.43	11.01	5.79	127-129 (0.8)
7 and 8	C ₁₂ H ₁₇ N ^a	82.23	9.78	7.99	82.22	9.64	8.07	66-68 (0.2)
12	C ₁₂ H ₁₅ N	83.19	8.73	8.09	82.98	8.79	8.02	68-70 (1.5)
11 and 13	C ₁₄ H ₁₉ N ^b	83.53	9.51	6.96	83.59	9.58	6.81	107-109 (0.5)
14	C ₁₅ H ₂₁ N	83.66	9.83	6.51	83.49	9.78	6.61	119-121 (0.8)
15	C ₁₄ H ₁₉ NO	77.38	8.81	6.45	77.11	8.89	6.43	126-128 (0.8)
16	C ₁₆ H ₂₃ NO	78.32	9.45	5.71	78.54	9.65	5.64	127-129 (0.8)
17	C ₁₅ H ₂₂ N ₂	78.21	9.63	12.16	78.28	9.75	12.01	133-135 (0.8)
18	C ₁₆ H ₂₅ N	83.05	10.89	6.05	83.12	10.98	6.02	112-114 (0.8)
19a or 19b	C ₁₇ H ₂₆ N	83.89	10.35	5.76	83.67	10.46	5.62	145-147 (0.9)
20a or 20b	C ₁₇ H ₂₆ N	83.89	10.35	5.76	83.90	10.36	5.73	136-138 (0.2)
21a or 21b	C ₂₀ H ₃₁ N	84.14	10.95	4.91	84.04	11.13	5.15	163-165 (0.6)
22	C ₁₈ H ₂₇ N	83.99	10.57	5.44	84.18	10.83	5.52	151-153 (0.5)
23	C ₁₈ H ₂₇ N	83.99	10.57	5.44	84.03	10.23	5.68	147-149 (0.3)
24	C ₁₉ H ₂₉ N	84.07	10.77	5.16	84.26	10.91	5.00	180-182 (2.0)

^a This sample is a mixture of 7 and 8 in a ratio of 16:1. ^b This sample is a mixture of 13 and 11 in a ratio of 11:1.

of 6.5 g (0.05 mol) of **3** in 10 ml of hexane was next added over a period of 10 min. The reaction mixture was stirred for 12 hr at 25°. This reaction gave 7.25 g (64%) of **4** and 1.6 g (35%) of unreacted **3**.

Reaction of 1,2-Dihydronaphthalene (3) by Means of *n*-Butyllithium and Thiophenol.—To 80 ml of thiophenol contained in a reaction flask equipped with condenser, nitrogen inlet tube, stirrer, and an addition tube, 30 ml of an 8% solution of *n*-butyllithium-hexane was added over a period of 15 min. A white precipitate formed. To the stirred suspension, 3.25 g (0.025 mol) of **3** was added, and the reaction mixture was stirred at 25°. After a 12-hr period, the reaction mixture was diluted with water and treated with 10% sodium hydroxide solution. This basic solution was extracted with ether and the ether extract was steam distilled to remove unreacted **3** (1.5 g, 48%). The residue from the steam distillation was extracted with ether, dried (MgSO₄), and concentrated to 4.0 g of crude dark oil. Evaporative distillation gave 2.92 g (48%) of **36**: nmr (CDCl₃) δ 7.19 (m, 5, ArH), 6.92 (s, 4, ArH), 3.32 (m, 1, CH adjacent to S), 2.88 and 2.72 (m, 4, ArCH₂), and 1.99 (m, 2, -CH₂- nonbenzylic and not adjacent to S); mass spectrum (70 eV) *m/e* (rel intensity) 240 (34), 131 (100), 130 (71), 129 (39), 115 (29), and 91 (28).

An ether-insoluble, ethyl-acetate-soluble product, mp 59-60°, weighing 1.8 g, was isolated. This was identified as diphenyl di-

sulfide by comparison with authentic material through melting point and mass nmr spectra.

Registry No.—**4**, 23853-47-6; **5**, 23853-48-7; **6**, 23853-49-8; **7**, 19485-86-0; **8**, 23853-51-2; **11**, 23853-52-3; **12**, 23853-53-4; **13**, 23853-54-5; **14**, 23853-55-6; **15**, 23853-56-7; **16**, 23853-57-8; **17**, 23853-58-9; **18**, 23853-59-0; **19a**, 23853-60-3; **19b**, 23890-38-2; **20a**, 23853-61-4; **20b**, 23853-62-5; **21a**, 23853-63-6; **21b**, 23853-64-7; **22**, 23853-65-8; **23**, 23853-66-9; **24**, 23853-67-0; **36**, 23853-68-1.

Acknowledgments.—We are grateful to the American Petroleum Institute for support of API Research Project 58A and to the Research Foundation, Oklahoma State University, for their assistance. We thank Dr. O. C. Dermer for valuable discussions and for having read the manuscript. We are also grateful to the National Science Foundation for support through Grants GY-2420 and 68098.